PB86-219391

# Quantities of Cyanide-Bearing and Acid-Generating Wastes Generated by the Mining and Beneficiating Industries, and the Potentials for Contaminant Release

Versar, Inc., Springfield, VA

Prepared for

Environmental Protection Agency, Washington, DC

27 Jun 86

**U.S. Department of Commerce**
**National Technical Information Service**
NTIS

PB86-219391

# FINAL REPORT

# Quantities of Cyanide-Bearing and Acid-Generating Wastes Generated by the Mining and Beneficiating Industries, and the Potentials for Contaminant Release

EPA Contract No. 68-01-7090
Assignment No. F-12

and

EPA Contract No. 68-01-7053
Assignment No. 42.4

Prepared for:

U.S. Environmental Protection Agency
Economics Analysis Branch
Office of Solid Waste
401 M Street, S.W.
Washington, D.C. 20460

Prepared by:

Versar Inc.
6850 Versar Center
Springfield, Virginia 22151

June 27, 1986

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

50272-101

| | | | |
|---|---|---|---|
| **REPORT DOCUMENTATION PAGE** | **1. REPORT NO.** EPA/SW/530-86/025 | **2.** | **3. Recipient's Accession No.** PB86 219391/AS |

**4. Title and Subtitle** Quantities of Cyanide-Bearing and Acid-Generating Wastes Generated by the Mining and Beneficiating Industries, and the Potentials for Contaminant Release

**5. Report Date** 06/27/86

**6.**

**7. Author(s)**

**8. Performing Organization Rept. No.**

**9. Performing Organization Name and Address**
Versar, Inc.
6850 Versar Center
Springfield, VA 22191

**10. Project/Task/Work Unit No.** F-12/42.4

**11. Contract(C) or Grant(G) No.**
(C) 68-01-7090-68-01-7093
(G)

**12. Sponsoring Organization Name and Address**
Office of Solid Waste, EPA
401 M Street, S.W., WH-562
Washington, D.C. 20460

**13. Type of Report & Period Covered** Final

**14.**

**15. Supplementary Notes**
Prepared in support of the Regulatory Determination on Mining Wastes (51 FR 24496; (July 3, 1986)

**16. Abstract (Limit: 200 words)**

This report identifies the cyanide and acid wastes associated with the extraction or concentration of metals from ores. The cyanide-bearing wastes covered are related to keep and vat leaching operations in the gold and silver industries. The wastes generating sulfuric acid are found in several metal mining sectors. However, the report focuses on the operations using surfuric acid (largely generated from iron sulfides) to leach copper from dumps and estimates the acid generation potential for will tailings accumulated in impoundments. Types of releases are identified but not quantified. The report concludes that data on release rates must be acquired on a site-specific basis.

**17. Document Analysis a. Descriptors**

**b. Identifiers/Open-Ended Terms**

**c. COSATI Field/Group**

| | | |
|---|---|---|
| **18. Availability Statement** | **19. Security Class (This Report)** Unclassified | **21. No. of Pages** |
| | **20. Security Class (This Page)** Unclassified | **22. Price** |

(See ANSI–Z39.18)

See Instructions on Reverse

OPTIONAL FORM 272 (4–77)
(Formerly NTIS–35)
Department of Commerce

## TABLE OF CONTENTS

Page No.

EXECUTIVE SUMMARY ........ EX-1

1. INTRODUCTION ........ 1-1
   - 1.1 Background ........ 1-1
   - 1.2 Purpose and Scope ........ 1-1
   - 1.3 Data Limitations and Conclusions ........ 1-2
     - 1.3.1 Cyanide-Bearing Wastes ........ 1-2
     - 1.3.2 Wastes with Acid Generation Potential ........ 1-4

2. CYANIDE-BEARING WASTES ........ 2-1
   - 2.1 Identification of Types of Cyanide-Bearing Wastes. ........ 2-2
     - 2.1.1 Vat Leaching Wastes ........ 2-5
     - 2.1.2 Heap Leaching Wastes ........ 2-6
   - 2.2 Quantification of Cyanide-Bearing Wastes ........ 2-9
     - 2.2.1 Historical Rates of Waste Production ........ 2-9
     - 2.2.2 Assessment of Future Waste Production Rates ........ 2-17
     - 2.2.3 Estimated Total Potential Cyanide Present in Mining Wastes ........ 2-19
     - 2.2.4 Quantification of Concentrations of Cyanide in Various Types of Wastes ........ 2-22
     - 2.2.5 Conclusions ........ 2-42
   - 2.3 Environmental Fate, Releases, and Transport of Cyanides ........ 2-44
     - 2.3.1 Assessment of Data on the Potential for Cyanide Releases ........ 2-44
     - 2.3.2 Assessment of Data on Cyanide Fate and Transport ........ 2-55
     - 2.3.3 Assessment of Reported Data on Releases ........ 2-71
       - 2.3.3.1 Heap leaching Sites and Releases of Cyanide ........ 2-75
       - 2.3.3.2 Vat Extraction Sites and Releases of Cyanide ........ 2-79
     - 2.3.4 Treatment of Cyanide-bearing Wastes ........ 2-87
     - 2.3.5 Conclusions ........ 2-88

3. ACID GENERATING WASTES ........ 3-1
   - 3.1 Identification of Acid Generating Mine Wastes ........ 3-1
     - 3.1.1 Mine Development Wastes ........ 3-4
     - 3.1.2 Milling Wastes (Tailings) ........ 3-5
     - 3.1.3 Copper Dump Leach Wastes ........ 3-6

TABLE OF CONTENTS (continued)

Page No.

3.2 Mine Waste Volumes and Qualitative Assessment of Acid Generation Potential........................ 3-9
3.2.1 Mine Development Wastes.................... 3-9
3.2.2 Tailings from Ore Beneficiation............ 3-13
3.2.3 Copper Dump Leach Wastes................... 3-38
3.3 Semi-Quantitative Estimate of Total Acidity Contained in Mine Wastes.......................... 3-44
3.4 Assessment of Future Waste Generation Rates........ 3-49
3.4.1 Copper.................................... 3-50
3.4.2 Lead...................................... 3-52
3.4.3 Zinc...................................... 3-54
3.5 Methods for Assessing Acid Generation and Release Rates............................................ 3-55
3.5.1 Acid Formation............................ 3-56
3.5.2 Removal Mechanisms........................ 3-60
3.5.3 Conclusions............................... 3-70

4. REFERENCES.............................................. 4-1

## Disclaimer

This document has been reviewed and approved for publication by the Economic Analysis Branch, Office of Solid Wastes, U.S. Environmental Protection Agency. The use of trade names or commercial products does not constitute Agency endorsement or recommendation for use.

## LIST OF TABLES

| | | Page No. |
|---|---|---|
| Table 2-1 | Summary of Mill Tailings for Gold-Silver Mining | 2-12 |
| Table 2-2 | Percentage of Gold Recovered from All Sources by Different Processes.......................... | 2-13 |
| Table 2-3 | Percentage of Silver Recovered from All Sources by Different Processes.......................... | 2-14 |
| Table 2-4 | Spent Ore Resulting from the Cyanidation Process in the United States............................ | 2-16 |
| Table 2-5 | Twenty Year Projection (1982-2001) of Mill Tailings Produced from Gold-silver Ores......... | 2-18 |
| Table 2-6 | Free Cyanide Concentrations in Eleven Locations in the Darwin Heap.............................. | 2-25 |
| Table 2-7 | Total Cyanide Concentrations for Various Heap Leach Operations in California................. | 2-26 |
| Table 2-8 | Results of Tests with Cyanide Solutions (in ppm)[a] Added to Columns Containing Native Soil from the Area of Annie Creek Mine, SD.................... | 2-30 |
| Table 2-9 | Cyanide Levels (ppm) in a Vat Tailings Pond Sampled One and Three Months After Closure....... | 2-32 |
| Table 2-10 | Tailings Pond Influent and Effluent Concentrations at Dome Mines Limited, Timmins, Ontario.......... | 2-34 |
| Table 2-11 | Data from ERCO (1984) Mining Waste Study......... | 2-35 |
| Table 2-12 | Data from PEI (1983) Mining Waste Study......... | 2-37 |
| Table 2-13 | Effluent Concentrations (mg/l) for Some Typical Canadian Gold Mill Tailings, as Reported by Scott (1985)............................... | 2-38 |
| Table 2-14 | Cyanide Concentrations (in ppm) in a Carbon-in-Pulp (CIP) Cyanide Mill Tailings Pond in Western Australia........................................ | 2-41 |

LIST OF TABLES (continued)

Page No.

Table 2-15 Concentrations (mg/l) of Cyanides in Some Typical Canadian Gold Mill Barren Bleed Solutions, as Reported by Scott (1985).......... 2-43

Table 2-16 Relative Stability of Cyanide Complexes......... 2-46

Table 2-17 Cumulative Constants, $B_n$, for Various Metals Found in Precious Metal Ores.................... 2-49

Table 2-18 Degradation of Metallocyanide Complexes in Phosphate Buffer at pH 7......................... 2-52

Table 2-19 Summary of Environmental Fate and Transport of Cyanides from Mining Wastes.................. 2-56

Table 2-20 Relationship of pH to Percent HCN in Free Cyanide ($CN^-$ plus HCN) of an Aqueous Solution.. 2-60

Table 2-21 Materials Received from Various Submitters Concerning Cyanide-Bearing Mining Wastes......... 2-72

Table 3-1 Sulfidic Minerals That Oxidize to Form Sulfuric Acid............................................ 3-2

Table 3-2 Mine Development Waste and Waste to Ore Ratios for Mining Segments Commonly Associated with Pyritic Ores.................................... 3-12

Table 3-3 Tons of Copper, Lead, Zinc, Gold Ore Concentrated or Vat Leached from 1910 to 1981; Source; Mineralization; and Acid Generation Potential........................................ 3-14

Table 3-4 Ore Processed by Concentration and Vat Leaching for the Period 1982 Through 1984 3-28

Table 3-5 Data Indicating Acid Generation by Ore or Tailings, Compared to Assessed Acid Generation Potentials for Associated Ore Bodies........... 3-36

## LIST OF TABLES (continued)

| | | Page No. |
|---|---|---|
| Table 3-6 | Known Tons of Ore in Copper Leach Dumps, Associated pH Data, and Acid Generation Potentials | 3-39 |
| Table 3-7 | Total Potential Acidity of Wastes (Where Quantifiable) | 3-47 |
| Table 3-8 | Minimal Data Requirements for Estimation of Water Flux Through and Seepage From Waste Piles. | 3-64 |
| Table 3-9 | Summary of Potential Surface Impoundment Catastrophic Failure Mechanisms | 3-67 |
| Table 3-10 | Data Requirements for McWhorter and Nelson Impoundment Seepage Model | 3-68 |

## LIST OF FIGURES

Page No.

Figure 2-1 Cyanide Degradation Model (Simovic et al. 1984; Simovic and Snodgrass 1985) .................... 2-81

Figure 3-1 Generalized Flowsheet for Copper Dump Leaching Operations .................................... 3-7

Figure 3-2 Solubilities of Oxides and Hydroxides of Various Metals ................................ 3-10

Figure 3-3 Estimated Cumulative Tons of Ore with High or Intermediate Acid Generation Potential Mined and Milled 1910-1981 .......................... 3-30

# EXECUTIVE SUMMARY

This report documents the initial phases of a human exposure and ecological impact assessment of mining and beneficiation wastes bearing cyanides or generating acids. This assessment will serve as an important technical input to the decision of whether to promulgate regulations for these wastes, to be made by USEPA in June of 1986 as mandated by Section 3001 of the Resource Conservation and Recovery Act (RCRA).

The first step in exposure/ecological impact assessment is the quantification of hazardous constituent release from wastes to the surrounding environment. This is followed by environmental fate and transport assessments leading to ambient concentration estimation; identification of exposed human and biotic populations; and estimation of dose incurred by exposed populations. Human risk is subsequently assessed based on dose estimates and constituent toxicity, while ecological impact is assessed based on the known ecotoxicity of associated constituents. As the initial phase in this process, the project that this report documents had as its goals to assemble and review the data available in published sources and from the U.S. Bureau of Mines (USBM), and to assess the feasibility of developing with these data a nationwide source term for releases of acids and cyanides from mining and beneficiation wastes.

Pertinent data in the reviewed literature, largely regarding waste quantities but including limited information on the cyanide concentrations and acid formation potential of these wastes, were extracted and are summarized in this report. Data requirements for source term development are reviewed, data gaps are identified, and suggestions for further data generation and assessment are presented.

Data sources accessed in this project include:

- A large body of analytical data on mining wastes developed and contained in reports by PEI (1983) and ERCO (1984).
- Numerous references published by USBM containing compilations of pertinent data (especially, Minerals Yearbook, Coppa (1984), Mineral Facts and Problems series).
- Several reports prepared for or published by USEPA (especially USEPA Mine Wastes Report to Congress).
- The USBM Minerals Availability System data base.
- Numerous contacts with experts in the field, including those in U.S. Government agencies, U.S. Universities, and Canadian agencies.
- About fifteen studies provided to Versar by precious metals mining companies concerning cyanide-bearing wastes.

Several comprehensive treatises on ore body composition and numerous published journal articles and texts identified through automated literature searches were also reviewed. The scope of this project did not include contacting the mining industry, although about 10 precious metals mining companies provided information to EPA and/or Versar.

Cyanide-bearing mining and beneficiation wastes assessed in the project include those resulting from the cyanidation of precious metal ores. Wastes assessed for acid formation potential include those with high sulfide content (and, therefore, likely to release acid as a result of sulfide oxidation) and wastes from the acid leaching of copper at dump leach operations.

Available data regarding the historical and/or cumulative, present annual, and projected future wastes likely to contain cyanides and acids are summarized in this report. A total of approximately 300 million metric tons of tailings from the beneficiation of gold and silver ores have been generated since 1910. This figure includes wastes generated by all milling processes, however, and only an unquantifiable portion of these tailings were from cyanidation processes. Data specifically for cyanidation wastes are available beginning in 1974. These data indicate that through the combined vat and heap leach cyanidation of gold ores, about 30 million metric tons of spent ore were generated in the 6 years between 1974 and 1979 and about 97 million metric tons of spent ore were generated in the 5 years from 1980 to 1984; for silver ores, in the 6 years from 1974 to 1979, about 18 million metric tons of spent ore were generated by the combined vat and heap leaching with cyanide, while 71 million metric tons of spent silver ores were generated in the 5 years from 1980 to 1984. Thus, in the last few years there have been large increases in the cyanidation processing of precious metal ores.

Approximately 29 million metric tons of gold ore and about 24 million metric tons of silver ore were treated by cyanidation in 1984. Some ores containing both gold and silver are included in the above totals for both commodities; thus, the total ore treated by cyanidation is less than the total of the above two figures.

It has also been estimated that 420 million metric tons of tailings will be generated from the combined beneficiation of gold and silver ores from 1982 to 2001. This projection includes tailings from other precious metal ore beneficiation processes in addition to cyanidation, however.

Data for the years 1979 through 1984 indicate that the rate of increase in vat leaching of precious metal ores was slower than the rate of increase of heap leaching. In 1984 over 1.5 times as much gold and silver ore was processed by heap leach cyanidation as was processed by vat leaching, and this ratio is expected to increase. This is because of the greater cost-effectiveness of heap leaching in extracting precious metals from lower grade ores. The increase in mining and heap leaching of lower-grade ores may be expected to result in further increases in the ratio of waste produced per metal extracted.

A common rule of thumb is that approximately 1 pound of cyanide is applied per ton of ore in a gold heap leach operation. Using this factor, it is estimated that nearly 20 million pounds of cyanide were applied to gold heap leaching sites nationwide in 1984. No similar rule of thumb is available for vat cyanidation operations, or for heap-leaching of silver ores, which are not included in this estimate, and add significantly to the amount of cyanide used by the metals mining and beneficiating industry annually.

Mining and benefication wastes with acid generation potential are broken down into three categories: mine development waste (material removed in accessing the ore body to be mined); mill tailings (spent ore material resulting from beneficiation); and copper dump-leach wastes. Data regarding tons of mine development waste produced by metal mining segments associated with pyritic ores (i.e., ores with high sulfide content and therefore acid generation potential; largely of the ores, copper, lead, zinc, silver, gold) are available beginning in 1974. It is estimated that a total of approximately 2.7 billion metric tons of mine development waste were generated by these industries during the period 1974 through 1983. Annual waste generated in 1983 exceeded 310 million metric tons, and it is projected that the copper, lead, and zinc mining industries alone will produce over 4.9 billion metric tons of mine development waste in the period 1984 through the year 2000. These figures include wastes from both pyritic and non-pyritic ores; the two categories cannot be distinguished with available data. Further, mine development wastes frequently are not pyritic even when associated with a pyritic ore body, and vice versa. Hence, the acid generation potential of these wastes could not be assessed with the data from reviewed sources.

Over 5 billion metric tons of tailings with high or intermediate acid generation potential were produced by the combined copper, lead, zinc, gold, and silver industries in the period 1910 through 1981. This represents roughly 64 percent of all tailings produced by these industries during this period. Tailings produced annually (1984) by the copper, gold, and silver segments exceeded 460 million tons. These 1984 data do not, however, allow distinction between high, intermediate, or low acid generation potential. It is estimated that over 5 billion metric tons of tailings will be produced by the copper, lead, zinc, gold, and silver industries in the period 1982 to 2001. Again, acid generation potential of these projected future tailings cannot be predicted, although by assuming that those tailings with high or intermediate acid generation potential will again equal roughly 60 percent of the total tailings produced, one can project that over 3 billion metric tons of acid-generating wastes will be produced during this period.

Data available do not allow accurate quantification of the total amount of ore and waste materials placed on copper leach dumps, although it is known that at least 5.5 billion metric tons of materials were in place on these sites as of 1983. At least 40 million tons of material are placed on copper dump leach sites annually (1983). It is known that these estimates for past and current annual dump leach material volumes represent a majority of all such materials; however, the total volumes cannot be accurately quantified with data available in the reviewed sources.

No reliable projection of future copper dump leach volumes could be made. Annual domestic primary production of copper is expected to increase by 35 percent by the year 2000, however, and copper dump leaching is expected to account for an increasing portion of primary copper production because of the lower unit production costs and amenability of the dump leach proces to processing lower grade ores.

All materials placed on copper leach dumps are considered to have at least intermediate acid generation potential after the closing of copper dump leach sites. This is because strong acid solutions are used as leach liquors at these sites during operation, and many sites include highly pyritic materials.

The chemical characteristics and, therefore, the cyanide concentration or total acid generation potential of these wastes is highly variable and specific to individual sites. Limited empirical data regarding cyanide concentration in wastes were available in the reviewed literature and the submitted reports. Available data, tabulated in this report, indicate total cyanide concentrations ranging from over 150 mg/kg to below detection limits in spent heap leach wastes, and from over 800 mg/kg to less than 2 mg/kg in tailings pond waste materials. These data generally do not indicate the chemical form of the cyanides present, an important factor in defining cyanide mobility and toxicity. Limited data available indicate that a significant portion of cyanides present are strongly complexed, and therefore are not very mobile or toxic to humans.

Cyanide present in these wastes degrades both biologically and chemically at varying rates; degradation rates have been measured at one heap leach site, two tailings ponds and a barren bleed pond. Based on tailings and barren bleed pond measurements, a model has been developed for estimating the rate of cyanide degradation in tailings ponds. Additional data are required, however, before this model can be verified and before the rate of cyanide degradation in mining and beneficiating wastes can be reliably quantified. It is expected that degradation processes result in significant reductions in cyanide concentrations in older wastes.

Net potential acidity (i.e., acidity exceeding the natural neutralizing capacity of the soil) present in pyritic ore bodies mined for metals is estimated and tabulated where data permit. These estimates, which are semi-quantitative at best, indicate that net potential acidity ranges as high as 80 percent (as $CaCO_3$ equivalents) but is most commonly around 5 percent (as $CaCO_3$) for ore bodies judged to have acid generation potential.

This net potential acidity figure does not, however, provide an indication of the rate of acid generation, which ultimately determines the environmental impact of releases from acid-generating wastes. Acid generation rates are highly variable, and are driven by numerous site-specific factors, which are discussed in this report. Acid generation rates vary greatly even within individual sites over time. Methods of measuring and predicting acid generation rates are available, and are summarized in this report. However, these methods have yet to be widely applied. Data required for estimation of acid generation rates on a national basis are not presently available.

Releases of cyanides and acids from mining wastes may occur through runoff from waste piles during storm events; leaching of constituents from waste piles by infiltrating rainwater; seepage of constituents through the bottoms of tailings ponds and leach pad liners; and sudden, high-volume releases due to failure of tailings pond dams. While scattered data are available and are summarized herein regarding individual release incidents, data available from the accessed sources do not allow accurate quantification of release rates from mining wastes on a nationwide basis.

Because of the highly variable nature of surrounding topography, site geology, hydrology, climate, soil chemistry, and biology, a generalized model allowing release rate estimation based on limited parameters is not feasible. Source terms must be estimated on a site-specific basis. Data requirements for such site-specific estimations are extensive and are summarized in this report along with appropriate estimation methods.

As this report indicates, the total amounts of mining and beneficiation wastes containing cyanides or exhibiting acid generation potential, and the concentration of cyanides or the acid generation potential of a limited portion of these wastes, can be roughly quantified; however, a national source term for cyanide and acid releases from these wastes can only be developed through the acquisition of additional data. Because of the highly site-specific nature of the numerous factors determining cyanide or acid releases, data for source-term estimation must be acquired on a site-specific basis. Data requirements are extensive. An alternative approach to human exposure and ecological impact assessment, that of obtaining empirical ambient concentration data within the impact area of mining and benefication waste releases (which can be substituted for the results of source term and environmental transport/fate assessment), is one of the viable, suggested alternatives to collecting large amounts of data and estimating the nation-wide source terms.

# 1. INTRODUCTION

## 1.1 Background

This report is the result of initial technical investigations performed by Versar under contract to the EPA Office of Solid Waste Economics Analysis Branch (EAB). The associated project is a part of an overall EAB work plan for developing information that will serve as the basis for a regulatory determination to be made by EPA regarding wastes from metals mining and beneficiation. The Resource Conservation and Recovery Act (RCRA) requires that EPA, within six months of publication of the Report to Congress regarding these wastes (published on December 31, 1985), either (a) promulgate regulations for these wastes or (b) determine that such regulations are unwarranted.

The overall EAB work plan includes human risk and ecotoxicological assessments regarding each category of metals mining and benefication wastes. This report represents the initial stage of such assessments for two waste categories.

## 1.2 Purpose and Scope

Steps in human risk and ecotoxicological assessment include quantification of hazardous substance release from metals mining and beneficiation wastes (i.e., source term development); assessment of the transport and fate of released contaminants in the environment; quantification of ambient concentrations of contaminants; identification of points of exposure and exposed biota, ecological communities, and human populations; assessment of ecological impact based on exposure levels; quantification of dose incurred by exposed human populations; and assessment of human health risks associated with the incurred doses, based on contaminant toxicological properties. The purpose of the project under which this present report was prepared is to conduct the initial stages of source term development. The scope of this project is limited to those wastes bearing cyanides and those wastes that have a potential for generation of acids.

Available data regarding cumulative amounts of waste at metals mining and beneficiation sites, amounts currently generated, and amounts projected to be generated in the future were assembled, and where data were adequate these amounts were quantified. As available data permitted, the contaminant concentration or generation potential of these wastes were quantified, and total potential amounts of contaminants present at or generated by metal mining/beneficiation operations were assessed. Because of data constraints, this assessment was of necessity semi-quantitative. Pertinent methods of developing source terms were identified and outlined, and the feasibility of developing reliable contaminant source terms (i.e., rates of contaminant release to the environment) with currently available data was assessed. Data required for performance of source term analysis were identified.

The following is a summary of the outcome of the data assessment and conclusions regarding feasibility of source term analysis with presently available data.

## 1.3 Data Limitations and Conclusions

In the course of this data gathering and assessment effort, several significant limitations in data available from sources reviewed or contacted become apparent. These limitations are discussed in some detail in the pertinent individual sections and are briefly summarized here.

### 1.3.1 Cyanide-Bearing Wastes

(1) Data Limitations. There are significant gaps in cyanide-bearing mining wastes data available for quantification of the waste volumes and potential for environmental releases. These include the following:

- Quantities of cyanidation wastes. Cyanidation processing for precious metal extraction was introduced in the late 1800s, but data on the volumes of waste generated by cyanide leaching processes have been compiled by the Bureau of Mines only since 1974; the limited number of operations utilizing heap leaching prior to 1979 resulted in the heap-leaching vs. vat-leaching data being withheld by the Bureau of Mines and only composite cyanidation processing data were released for 1974 to 1978. No cyanidation processing data were available prior to 1974.

- Characteristics of cyanidation wastes. Except at very few sites, the levels of cyanides in waste materials have not been characterized. Both free cyanides and total cyanides are important parameters for characterizing the wastes. Determining the specific metallo-cyanide complexes present in both liquid and solid wastes would also be important for determining dissociation rates and potential releases.

- Degradation of cyanides in the cyanide-bearing wastes. The concept of cyanide degradation, both for metallo-cyanide complexes and for free cyanides, has been described in general terms, but limited information is available on cyanide degradation at actual waste disposal sites of spent heap leach ore and vat mill tailings.

- Potential release of cyanides. The potential pathways of cyanide release from disposal sites include runoff to surface waters, percolation into ground waters, and atmospheric releases. Solution losses may occur from leaking tailings ponds or heap leach pads or overflows during storms. Information on actual releases is sketchy, but this should not be inferred to suggest that releases do not occur.

- Mathematical models for predicting degradation within waste materials and releases from waste disposal sites. Two models are available to describe degradation of liquid waste (such as barren bleed solution and tailings wastes). These models might be applicable to spent heap leach ore with some refinements; model verification, however, has not yet been conducted for spent heap leach ore. There do not appear to be any other degradation models for spent heap ore. Models are available for predicting generic releases from solid and liquid waste materials, but there are limited input data for predicting environmental releases from cyanide-bearing wastes.

(2) Conclusions. The available information has been reviewed concerning the volumes of cyanide-bearing mining wastes, the concentrations of free and total cyanides in these wastes, and the potential releases of cyanide from mining waste sites. The data are presented in Section 2 of this report, but are inadequate for presenting quantitative assessments of releases. Thus, the source term for an exposure assessment is not adequate at this time. Without sufficient information for the exposure assessment, a risk assessment cannot be developed to characterize the potential environmental hazard and human health risk associated with cyanide-bearing wastes. The data available are highly site-specific, and more data are needed on cyanide levels in wastes, rates for each of the degradation processes, release rates, and exposure concentrations at points of human or biotic exposure.

### 1.3.2 Wastes with Acid Generation Potential

(1) Data limitations. Significant gaps in data identified and employed for quantification of wastes with acid-generation potential include:

- Quantities of mine development wastes. Data for quantities of rock and soil removed in order to access ore bodies have been maintained by the U.S. Bureau of Mines (USBM) only since 1978 and only in aggregation over entire commodities on an annual and national basis.

- Characteristics of mine development wastes. Data quantifying pyrite and carbonate contents of most ore bodies are available, but such data are available for overburden and waste rock at only a few specific sites. The total acid generation potential for mine development wastes could not be assessed.

- Quantities of ore placed in copper dump leach operations for some mines and for some years. While a great deal of such quantity data is available, significant gaps remain in the USBM data for these quantities.

- Characteristics of copper dump leach wastes and floatation mill/vat leach tailings. While the characteristics of ore bodies from which these wastes originated are available, the effect of leaching or processing on these characteristics could not be quantified. Such effects on waste characteristics were disregarded in assessment of total potential acidity of these wastes.

- Data allowing prediction of rates of acid generation from mine wastes. Such data, including numerous physical, chemical, and biological characteristics of the waste material, or the results of simulated weathering tests, are highly waste-specific and generally unavailable.

- Physical and hydrogeological parameters for waste disposal facilities/sites and their surroundings. These data are required for the estimation of water-borne transport of acids from waste sites. Portions of the required data are available in standard Soil Conservation Service and National Oceanic and Atmospheric Administration references. However, other data categories are highly site- and waste-specific.

(2) Conclusions. Data available in the reviewed literature are adequate for a semi-quantitative assessment of total potential acidity of a portion of cumulative wastes. This assessment is presented in Section 3 of this report; it covers approximately 17 percent of tailings wastes generated since 1910 that have acid generation potential and approximately 1 percent of copper leach dump wastes.

Quantifying national source terms for acid released from these wastes is not feasible with the data available in the reviewed literature or from contacted sources. Such data are highly site-specific in nature, and the data requirments for each individual site are extensive. The effort required to assemble and analyze such data for sites of sufficient numbers and diversity to represent the industry as a whole would be significant.

In view of the above, an alternative method should be considered for the development of release rate and ambient concentration data for risk assessment purposes; the method would involve surveying receiving water bodies and developing empirical ambient concentration data. Empirical data are more reliable than the results of estimation procedures and may be obtained for an expenditure of effort and resources similar to that required for collecting model input data.

# 2. CYANIDE-BEARING WASTES

Mining for precious metals in the United States was largely by placer methods in the early years. Placers are alluvial, marine, or glacial deposits containing particles of precious metals, especially gold. The deposits were worked by various hydraulic techniques and the gold recovered by gravity separation. In about 1890, the use of cyanide solutions was introduced for the leaching of precious metals from gold- and silver-bearing ores. Scott and Ingles (1981) and Coppa (1984) described one type of precious metal ore beneficiation, the flotation process, in which the precious metals are concentrated from finely ground ores by the selective adherence of mineral particles to rising bubbles. The flotation reagent contains a mixture of soda ash, a xanthate, and a frother (Coppa 1984). The concentrate resulting from the floatation process is collected, and at some sites these flotation tailings are further processed by cyanidation or might be sent to a smelter. Various other metal ores are also treated by flotation with reagents containing cyanide, but the residual tailings apparently contain only relatively smaller amounts of cyanide (for example, see the data of ERCO in Table 2-11 and PEI in Table 2-12 for floatation mills); thus the cyanide in flotation tailings for other types of ores are not of significant interest compared with cyanide-bearing wastes from precious metal ores.

Another cyanidation process introduced in the late 1800s involves the use of relatively strong cyanide solutions to leach the precious metals from the ores. For efficient leaching, the ore is broken into chunks and/or further crushed, and the precious metal should occur as free, fine-sized particles in an ore that does not contain cyanicides (materials that react with the cyanide, such as sulfides in the ore), impurities (materials that bind to the cyanide and inhibit the dissolution of precious metals, such as iron in the ore), and carbonaceous materials (which would resorb or prematurely precipitate the precious metal-cyanide complexes). If these cyanicides or impurities are present, leaching would not be used as the primary recovery process. For some pyrite ores, roasting or other pretreatment processes are used to oxidize the sulfur to drive off $SO_2$. Thus, the composition of the ore would be changed, the gold would no longer be encapsulated by the pyrite, and cyanide leaching would proceed efficiently.

For many years, cyanidation leaching was carried out in vats, tanks, or closed containers. In the late 1960s and early 1970s, the U.S. Bureau of Mines conducted research which indicated that open heap leaching could also be an economical process for the extraction of precious metals from certain low-grade ores, as well as from waste rock dump piles at old mines and previously discarded slimes tailings from old mills.

The waste materials, both solid and liquid, generated by active and abandoned vat and heap leaching operations may contain substantial levels of cyanides, and there is a potential for release of cyanide from these waste materials. The characterization and quantification of these cyanidation wastes, and descriptions of potential for releases, are the topics that will be discussed in this report. Atmospheric releases will also be described where appropriate. A review of the information currently available has identified various categories where existing data are limited or lacking, and these categories are also described.

## 2.1 Identification of Types of Cyanide-Bearing Wastes

Precious metal ores are mined from subsurface mines and from open pits. Because only lower grades of ores currently remain in place at most mines and pits and because of the large quantities of ore required for a commercially successful operation, leaching is usually conducted very near the source of the ore. Trucks or conveyors are used at a few locations to transport the ore from the mine to the vats or heap pads.

For efficient leaching of ores, crushing and grinding of the ore must be performed. It is most efficient to use very small particles of ore for vat leaching, but if the particles in a heap leach operation are too small, there may be clogging of pore spaces, resulting in channeling and inefficient leaching of the ore. One technique in heap leaching involves agglomeration of the fines onto coarser particles. Water may be added to the ore being built into the heap to agglomerate the fines, or lime or cement may be mixed with the ore and cyanide solutions added to stimulate the leaching process (McClelland and Eisele 1982).

The cyanide ion is composed of two atoms, carbon and nitrogen, joined by a triple bond. Cyanides are true ionic compounds ($CN^-$ is one of the few radical ions), and may complex with both organic and inorganic compounds. The basic species of the cyanide radical ($CN^-$) reacts with positive ions to form stable complexes. Most metals form positive ions, so they may readily react with the negatively charged ion. At pH values of less than about 9, the hydrogen cyanide species predominates and this form is volatile, so leaching is conducted at alkaline pHs (9.5 to 11) and lime ($CaO$ and/or $CaCO_3$) or caustic soda ($NaOH$) is added to control the pH (Chamberlain and Pojar 1984). Oxygen must be present for cyanide solutions to solubilize the free gold and silver (and other metals) as the complexed metallo-cyanide forms; this oxygen requirement places some constraints on the sizes of heaps that can be built for efficient heap leaching (Chamberlain and Pojar 1981).

DuPont is reportedly the only U.S. producer of sodium cyanide (NaCN) that sells the product to the ore beneficiation industry.* W.R. Grace also produces sodium cyanide (SRI 1985), but apparently uses the NaCN captively (production site-limited). There are a total of 14 locations where hydrogen cyanide is produced, but HCN is used captively at all but three sites; duPont Co., Memphis, Tennessee; Ciba-Geigy Corp.,

---

*Personal communication with F.W. DeVries, duPont Company, Wilmington, Delaware.

St. Gabriel, Louisiana; and Standard Oil Co., Lima, Ohio (SRI 1985). Because hydrogen cyanide is volatile, it is not the form used for ore beneficiation and precious metal leaching.

Intermountain Soils Inc. (1985) reported that one-half of the sodium cyanide sold in the U.S. is used for ore beneficiation, but that not all of the sodium cyanide is purchased from DuPont because some is imported from Canada, Europe, and Japan. Because DuPont is the sole U.S. manufacturer that sells sodium cyanide, their production data are held as confidential. Therefore, it is not possible to report their production or sales volumes or to estimate the amount of sodium cyanide used for ore beneficiation through production rate data.

The cyanide solution mixed with the precious metal ores is called the influent leaching solution. After the leaching process, the cyanidation forms metallo-cyanide complexes and the cyanide solution is called the pregnant solution, because of the dissolved precious metal values in the complexes. The pregnant solution is then processed by either zinc precipitation or activated carbon adsorption to separate out the precious metals. The cyanide solution remaining after these processing steps (called the barren solution) has high levels of residual cyanide ion and is recycled to a solution make-up tank for reuse in the cyanidation leaching operation. In addition to the barren solution that is recycled for its remaining leaching potential, some portion (the barren bleed solution) must be drawn off and discharged into a barren bleed pond to avoid elevated levels of metallo-cyanide complex impurities in the leaching cycle, impurities that would reduce the efficiency of both the leaching and the subsequent processing and separation of free gold and silver. These various terms and processes will be further described in subsequent sections describing cyanidation wastes.

### 2.1.1 Vat Leaching Wastes

Waste materials from the vat leaching cyanidation processes include both liquid and solid waste. In the past, specialized ores might have been treated in unusual ways, so the following general discussion describes the current situation more and is not a detailed retrospective. Vat leaching is characterized by fine grinding, high cyanide concentrations, agitation of leach materials, and leach times of a few hours to a few days. The precious metal ores are processed for vat leaching by crushing and grinding in autogenous, rod, or ball mill circuits to the size of fine particles, 80 percent of which are 200 mesh or smaller (i.e., 75 um holes in the mesh) (Hogan et al. 1982, Turk and Sass 1984). A NaCN and caustic soda (sodium hydroxide, NaOH) or lime (CaO) solution is added to the ore and may be mechanically mixed, agitated in Pachuca tanks, or air-agitated to obtain effective contact between the cyanide solution and the precious metal in the ore. Hogan et al. (1982) reported a vat-leaching cyanide solution concentration of 5,000 mg/l. The pregnant solution is drawn off the vat to recover the gold and/or silver. The recovery process involves either filtration with subsequent addition of zinc dust to precipitate the precious metal or adsorption onto activated carbon particles during countercurrent mixing followed by stripping with hot caustic soda, then electrowinning. The cyanide solution exiting from the recovery process would be recycled, but some may have to be sent to the barren bleed pond.

After the vat leach process is completed, the vat tailings are pumped as a slurry to a filtration unit where the tailings are washed with water in a primary filtration step to obtain any remaining metallo-cyanide complexes; countercurrent decantation is also used to wash the vat tailings. The tailings are then pumped to a tailings holding impoundment. Most of the recently constructed tailings impoundments have been lined with clay or synthetic liners and built behind earthen dams as zero-discharge impoundments. Because of rainfall and the residual moisture in the tailings, some new impoundments have drainage systems at the bottom of the impoundment to reduce the hydraulic head on the liner and to facilitate future leaching of the tailings if precious metal values are subsequently found to be economically recoverable. Later sections will discuss the volumes of tailings materials generated (Section 2.2.1), measured cyanide concentrations reported in tailings ponds (Sections 2.2.2(2)), and the potential for releases to air and water, both discharges to surface water and as ground water percolation (Section 2.3.3).

### 2.1.2 Heap Leaching Wastes

Chamberlain and Pojar (1981, 1984) and Intermountain Soils, Inc. (1985) have reported recent developments in the state-of-the-art of heap leaching. Based on information in their reviews and other literature sources, cyanide-bearing waste materials generated from heap leaching operations include liquid and solid waste, and there is a potential for releases to the atmosphere.

By definition, heap leaching operations are constructed upon an impervious base. "Dump leaching" is performed on materials such as waste rock piles and without a specially prepared base, and "in-situ" leaching is performed on the ore bodies in place with the cyanide solution sprayed on the surface and collected in recovery wells. The Carlin mine in Nevada is developing a gold ore dump leach operation, but according to Chamberlain and Pojar (1984) there are no other dump leach or in-situ leach operations for precious metals in the U.S. Dump and in-situ leaching are only very rarely used because of the values of the precious metals leached and the costs of cyanide in the leach solution.

The leach pads are constructed of compacted clay, synthetic products such as chemically-resistant plastics, or asphalt or tar materials

(Chamberlain and Pojar 1984). The pads are constructed with a gentle slope (2 to 5 percent) to collect the leachate which percolates down through the heap; this pregnant solution flows via a lined trough to the lined pregnant solution basin.

The heaps themselves vary in size depending on the grade of the ore, the size of the ore body, and the space availability at the site. Some new heaps in the Western United States are tens of acres in area. Sites having very limited areas of gently sloping terrain might involve reuse of the heap pad, while at sites where area is not a constraint, new pads may be constructed for each heap.

The size distribution of heap material ranges from run-of-mine fractured ores to particles of 0.25 inch (6 mm) (Chamberlain and Pojar 1984). Ore is spread by trucks, front end loaders, bulldozers, or conveyors onto lifts (layers) of 5 to 15 ft (2-5 m). Many heaps are built with multiple lifts. Chamberlain and Pojar (1984) present data on 26 heap leach operations in the Western United States and report a range of heap capacity from 2,000 to 500,000 short tons (1,814 to 453,500 metric tonnes). Much larger heaps, five times that size, are being planned or constructed.*

Chamberlain and Pojar (1984) reported that sodium cyanide is mixed with water at a strength of about 1 lb/ton of water (0.5 g/kg), to make a 0.05 percent solution (equivalent to about 250 ppm free cyanide). This is a lower cyanide concentration than that used in vat leaching. As with vat leaching, the alkaline pH of the leaching solution is maintained by adding caustic soda or lime to the solution.

The barren solution is sprayed on top of the heap via holes in pipes, lawn sprinklers, or Bagdad Wigglers. The droplets are large enough to minimize evaporation, and the spray volumes are low enough to avoid ponding on the surface of the heap. Solution application rates of about 1 to 100 gal/ft$^2$/day were reported by Chamberlain and Pojar (1984).

---

*Personal communication with E.H. Boyle, Jr., U.S. Bureau of Mines, Denver, CO.

For some ore types, heap leaching has been shown to be more efficient when the materials have been agglomerated with water or mixed with cement or lime in a cyanide solution prior to leaching. A successfully operating heap with proper solution percolation and leaching may continue to yield precious metal values for a few years of leaching. Because of freeze-up problems with sprinklers and solution holding ponds, heap leaching must be curtailed for a few months in the winter, although there are a few U.S. heap leach operations that utilize heated cyanide solutions and are able to use the leaching solutions year-round (for example, the Carlin heap leach and the Smoky Valley heap leach at Round Mountain, both in Nevada). The heap leaching season is shorter further north and at higher elevations; in fact, there are apparently no heap leach facilities operating in Canada.*

After precious metal values in the pregnant solution decrease to uneconomic levels, the leaching operation on the heap is terminated. Leaching time varies from site to site depending on ore grade and impurities, as well as other factors. At Smoky Valley Mining Co., in Central Nevada, the normal leaching cycle was expected to be 27 days for the leach solution sprinkling, 2 days for washing with water, and 2 to 3 days for drainage, for a total leach pad on-off cycle time of about 35 days (White 1977). At the Zortman and Landusky mines in Montana, the two 30-foot-high lifts each take about 30 days to complete, and the fully stocked heap leach pad is in a leach cycle for about three years before recovery values decline to a point where further cyanide application becomes uneconomic (Engineering and Mining Journal 1981a). Some heaps are left in place and new heaps built on adjacent land, or if the ore reserves at the site have been depleted, the site may be abandoned. If there are additional ore reserves at the site but limited space, the heap may be dismantled and the leach pad reused. At these sites, the spent ore would be dumped with the mine wastes (overburden) and/or the gangue (worthless rock from the precious metal ore body) or would be used to backfill the mine or pit. At the Carlin mine in Nevada, the spent ore from the heap leach site is dumped into the vat leach tailings impoundment, but this is not a typical disposition of spent ore since Carlin is one of the few mines in the U.S. with both a heap leach and a vat leach processing facility.

---

*Personal communication with L. Simovik, Environment Canada.

Chamberlain and Pojar (1984) reported that the gangue may consume as much as 25 to 50 percent of the cyanide applied. This cyanide, in the form of metallo-cyanide complexes (and contributing to analytical measurements of total cyanide), will remain in the spent ore, and might be subject to dissociation resulting in the release of free cyanide over a period of time. (Section 2.3.2 discusses some factors related to these dissociation reactions and releases).

The pregnant solution from heap leaching is stored in a lined pregnant solution basin until it is pumped to the precious metal recovery system at the site. Because of the values contained in the pregnant solution, the pregnant solution basins are constructed to minimize solution loss (Sections 2.3.1 and 2.3.2 describe the factors that may affect these releases).

## 2.2 Quantification of Cyanide-Bearing Wastes

### 2.2.1 Historical Rates of Waste Production

The mining of precious metal ores and extraction of the metals from the mined materials result in large volumes of wastes. The metal extraction processes result in both solid and liquid cyanide-bearing wastes. The ore mining from an underground mine or an open pit will result in waste rock, the overburden that must be moved aside in order to expose the ores that contain the precious metals. These waste rock materials, by definition, are not treated with cyanide, so they are beyond the scope of this section of the report.

Many developments in precious metal extraction have occurred during the life of existing large mines, and many abandoned lode mines contain ore grades that are now commercially attractive because of the price of the precious metals and recent advances in mining and milling technology. The consequences of these new methods and increased prices of gold and silver have created the following challenges for mining industry as described by Coppa (1984):

- The values in previously uneconomical ore deposits and even tailings dumps from old lode mines are now economically recoverable.
- Larger daily volumes of tailings must be handled because of lower ore grades, and can be handled economically because of the larger and more efficient ore moving, grinding, and processing equipment.
- Existing waste disposal facilities must be modified and expanded to accommodate increasingly finer-sized waste solids.
- Closed circuit disposal systems and/or cyanide destruction processes may be necessary to accommodate the large quantities of cyanide-containing waste waters.

The solid wastes generated by the extraction of metals are frequently termed "mill tailings" for vat leaching operations and "spent ore" for heap leaching operations. Heap leaching has become a major technological process only within about the last decade; historically, the cyanide-bearing wastes would have been generated by vat milling operations. Because of the types of solution mixtures utilized and the processes involved, froth flotation treatment of precious metal ores apparently results in very low levels of cyanide remaining in the floatation tailings. Most of the precious metal flotation reagents do not contain cyanide (Coppa 1984), and it is the flotation tailings that are processed by cyanidation (McQuiston and Shoemaker 1981).

Coppa (1984) presented data for mill tailings from gold-silver mining operations in each county in the United States, for each decade dating back to 1910. These mill tailings include solid wastes from all types of lode mine operations (except placers) and include waste ore processed at concentration mills, sent directly to smelters, or generated at mill operations (using amalgamation and/or cyanidation processes). These data were compiled into a composite table for the U.S. as a whole (Table 2-1). It was reported that a total of about 300 million metric tons of gold and silver mill tailings have been generated since 1910, but these waste volume data include other types of operations in addition to cyanidation. The data tabulated by decade for tailings generated reveal a pattern of cycles related to periods of economic depressions and government control of prices and laws against private ownership of gold.

Coppa (1984) also extracted data from various Bureau of Mines Minerals Yearbooks for each decade back to the 1910s to show the patterns of various extraction procedures for gold (Table 2-2) and silver (Table 2-3). Data in these tables reflect the increase in cyanidation for the extraction of precious metals during the last two decades; cyanidation has become the predominate method of extracting gold (Table 2-2). The recoveries of silver by cyanidation processes have increased, but smelting continues as the dominant method of silver recovery (Table 2-3).

The data in Tables 2-2 and 2-3 reflect the percentages of precious metals recovered by various processes, while the data in Table 2-1 are for volumes of mill tailings generated. The units are different, and the ore grades mined and processed have been declining, so it is not possible to directly use the data in these tables to derive estimates of the cyanide-bearing mining wastes currently generated.

Table 2-1. Summary of Mill Tailings for Gold and Silver Mining

| Period | $10^3$ Metric tons |
|---|---|
| 1910-19 | 64,557 |
| 1920-29 | 35,593 |
| 1930-39 | 58,254 |
| 1940-49 | 35,501 |
| 1950-59 | 20,088 |
| 1960-69 | 25,243 |
| 1970-81 | 59,815 |
| Total | 299,051 |

Source: Coppa 1984, as revised in personal communication with Lois Coppa 12/12/85.

### Table 2-2. Percentage of Gold Recovered from All Sources by Different Processes

| Year | Amalgamation | Cyanidation | Smelting | Placers |
|---|---|---|---|---|
| 1917 | 21 | 30 | 24 | 25 |
| 1926 | 31 | 20 | 29 | 20 |
| 1935 | 29 | 17 | 30 | 24 |
| 1947 | 18 | 13 | 37 | 32 |
| 1957 | 24 | 14 | 43 | 19 |
| 1967 | 25 | 39 | 32 | 4 |
| 1977 | 2 | 55 | 41 | 2 |
| 1981 | 1 | 66 | 31 | 2 |

Source: U.S. Bureau of Mines Minerals Yearbook, 1917, 1926, 1936, 1947 1957, 1967, 1977, 1981, as reported by Coppa (1984).

Table 2-3. Percentage of Silver Recovered from All Sources by Different Processes

| Year | Amalgamation | Cyanidation | Smelting | Placers |
|---|---|---|---|---|
| 1917 | .4 | 16.0 | 83.4 | .2 |
| 1926 | .3 | 8.0 | 91.6 | .1 |
| 1935 | .9 | 3.5 | 98.8 | .2 |
| 1947 | .2 | 0.8 | 98.8 | .2 |
| 1957 | .2 | 0.7 | 99.0 | .1 |
| 1967 | .3 | 0.2 | 99.5 | .02 |
| 1977 | .04 | 3.4 | 96.5 | .01 |
| 1981 | .005 | 11.0 | 88.9 | .1 |

Source: U.S. Bureau of Mines Minerals Yearbook, 1917, 1926, 1936, 1947 1957, 1967, 1977, 1981, as reported by Coppa (1984).

There have been recent advances in the technology of heap leaching with cyanide solutions to extract gold and silver. Since the mid-1970's, these have been large increases in the amounts of gold and silver ores treated by cyanidation (Table 2-4). U.S. Bureau of Mines data available for 1974 to 1978 do not distinguish between heap leaching and vat leaching, partly because of the confidentiality of data due to the limited number of heap leach operations. Table 2-4 shows that in 1979, the first year for which vat vs. heap leach data were readily available, about four times as much gold ore and two times as much silver ore were processed in vats, tanks, and closed containers compared with the respective volumes processed in open heaps and dumps. By 1981, a greater volume of ore was processed by heap leaching than in vat extraction. In 1984, the latest year for which data are available, almost two times as much spent ore was generated by heap leaching than by vat processing.

The total amount of ore treated by cyanidation cannot be obtained by addition of gold ore treated and silver ore treated. There is an overlap (duplication) because both gold and silver are recovered from some ores, but not all, thus explaining the differences between the data in Table 2-4 for total gold ore treated and total silver ore treated.

The ore processed by vat leaching usually is a higher grade than the ore that is heap leached. In 1984, only one-half as much gold was recovered by heap leaching (524,553 troy ounces of gold were recovered in heap leaching compared with 1,136,504 troy ounces from vat leaching) (Lucas 1985a), although almost twice as much ore was heap leached than vat leached (Table 2-4). Thus, simple calculations of the 1984 data indicate an average recovery of 0.094 troy ounces/short ton by vat leaching compared with an average recovery of 0.026 troy ounces/short ton by heap leaching; in 1979, the average recoveries for gold were 0.076 troy ounces/short ton for vat leaching and 0.038 troy ounces/short ton

Table 2-4. Spent Ore Resulting from the Cyanidation Process in the United States

| | Extraction in vats, tanks, and closed containers Gold ore treated (metric tons) | Leaching in open heaps or dumps Gold ore treated (metric tons) | Total gold ore treated by cyanidation (Metric tons) | Extraction in vats, tanks, and closed containers Silver ore treated (metric tons) | Leaching in open heaps or dumps Silver ore treated (metric tons) | Total silver ore treated by cyanidation (Metric tons) |
|---|---|---|---|---|---|---|
| 1974 | -- [a] | -- [a] | 4,069,262 [b] | -- [a] | -- [a] | 1,763,174 [b] |
| 1975 | -- | -- | 5,200,863 [b] | -- | -- | 2,053,192 [b] |
| 1976 | -- | -- | 3,659,290 [b] | -- | -- | 2,690,533 [b] |
| 1977 | -- | -- | 5,597,000 [b] | -- | -- | 3,539,613 [b] |
| 1978 | -- | -- | 4,411,224 [b] | -- | -- | 3,759,910 [b] |
| 1979 | 5,495,490 [c] | 1,464,829 [c] | 6,960,319 [c] | 2,916,232 [e] | 1,464,829 [e] | 4,381,061 [e] |
| 1980 | 7,137,322 [d] | 3,546,757 [d] | 10,684,079 [d] | 3,514,240 [f] | 3,074,792 [f] | 6,589,032 [f] |
| 1981 | 6,370,619 [d] | 8,049,980 [d] | 14,420,599 [d] | 4,022,395 [f] | 6,723,790 [f] | 10,746,185 [f] |
| 1982 | 6,907,745 [d] | 11,150,868 [d] | 18,058,613 [d] | 6,870,957 [f] | 11,151,684 [f] | 18,022,641 [f] |
| 1983 | 10,264,777 [d] | 14,673,929 [d] | 24,938,706 [d] | 8,469,321 [f] | 11,507,508 [f] | 19,976,829 [f] |
| 1984 | 10,941,930 [d] | 18,010,854 [d] | 28,952,784 [d] | 9,763,620 [f] | 14,312,997 [f] | 24,076,617 [f] |

Source: [a] -- not available.
[b] Moore 1986.
[c] Lucas 1984.
[d] Lucas 1985a.
[e] Reese 1984.
[f] Reese 1985a.

for heap leaching, based on data in the 1983 Minerals Yearbook (Lucas 1984). These recovery data suggest that the higher grades of ores are now being vat leached and lower grades of ores are being heap leached. The data trends also suggest that this pattern will continue, and that even lower grade ores and greater ore volumes may be heap leached in future years.

### 2.2.2 Assessment of Future Waste Production Rates

Estimates of future production of gold and silver by cyanidation depend on a number of factors, including the domestic price of the metals on the commodities market and usage patterns. In 1984, about 53 percent of the total U.S. gold consumption (not including monetary bullion) was used in jewelry and the arts, 35 percent was accounted for by industrial uses (electronic products, specialty alloys, and aerospace applications), and the remaining 12 percent in dental applications (Lucas 1985a,b). U.S. industrial consumption of silver declined in 1984 to its lowest level since 1963 (Reese 1985a). The decline in consumption of sterlingware and jewelry reflected the changing tastes of U.S. consumers as well as investment decisions based on higher monetary returns from other investments. The use of silver in electrical and electronic products also declined due in part to declining demand for personal computers and other prestige electronic products. The U.S. economy continued to recover, and silver consumption for photographic materials also increased, but declines in consumption for other uses offset increases in photographic uses, and there was a net decline in silver consumption. Industrial demand for gold and silver, however, exerts only slight influence over gold and silver prices.

Coppa (1984) used production trends in 1981 to predict mill tailings produced for gold and silver mining during the two decades beginning in 1982. The mill tailings projections were for gold and silver ores, but were not limited to cyanidation processes (Table 2-5). The data

Table 2-5. Twenty Year Projection (1982-2001) of Mill Tailings Produced from Gold-silver Ores[a]

| State and county | $10^3$ Metric tons |
|---|---|
| California: | |
| Calaveras | 6,335 |
| Idaho: | |
| Owyhee | 13,266 |
| Phillips | 3,811 |
| Valley | 3,672 |
| Total | 20,749 |
| Montana: | |
| Lincoln | 44,899 |
| Phillips | 38,999 |
| Granite | 2,000 |
| Total | 85,898 |
| Nevada: | |
| Elko | 11,250 |
| Esmeralda | 1,090 |
| Eureka | 27,199 |
| Humboldt | 8,909 |
| Lander | 18,799 |
| Mineral | 15,599 |
| Nye | 191,672 |
| White Pine | 8,700 |
| Total | 283,218 |
| South Dakota: | |
| Lawrence | 19,999 |
| Utah: | |
| Tooele | 9,520 |
| Utah | 140 |
| Total | 9,660 |
| Washington: | |
| Ferry | 192 |
| National total | 426,082 |

[a] Reported by Coppa (1984) and revised by Coppa (personal communication, December 12, 1985).

presented by Coppa (1984) suggest that gold and silver mining/milling over the two decades considered would result in the generation of more mill tailings than were provided in the previous five decades. Table 2-1 shows about 300 million metric tonnes were generated from 1910 to 1981, while Table 2-5 predicts that over 400 million metric tonnes will be generated from 1982 to 2001. In addition, the estimates in Table 2-5 were based partly on 1981 waste ore generation rates; however, Table 2-4 shows that almost twice as much gold and silver ores were treated by cyanidation in 1984 than in 1981. Thus, many caveats must be applied to any estimates of future amounts of spent precious metal ore generated by cyanide treatment, including the vagaries of world economic conditions; however, the increases in total mill tailings predicted by Coppa (1984) based on 1981 volumes are probably conservative based on 1984 cyanidation volumes.

An indirect source of projections of future spent ore is the Bureau of Mines' generation trends for gold and silver production based on annual forecasts of the industrial demand for gold (Lucas 1985b) and silver (Reese 1985b) for the year 2000. From a 1983 base, domestic demand for fabricated gold was forecast to grow at an average annual rate of 2.4 percent for the remaining years of this century (Lucas 1985b). Statistical projections for various end uses were developed based on the relation of past end-use patterns and historical and forecast data on macroeconomic indicators. The correlations were poor, however, because gold demand is heavily influenced by the wide fluctuations in the world price of gold, and affordability was considered as a contingency factor in preparing gold demand forecasts. The Bureau of Mines forecast (Reese 1985b) predicted that the demand for primary silver would show a probable average annual growth rate of 1.5 percent from 1983 to 2000. This forecast was significantly lower than previous silver consumption forecasts developed by the Bureau of Mines; they attributed the lower projections to recent silver price volatility and economic conditions which prompted manufacturers to reduce their reliance on silver by their development of more efficient methods for using the metal, development of substitutes, and development of improved methods for its recovery.

These Bureau of Mines forecasts and projections (Lucas 1985b, Reese 1985b) are based on the production and use of the precious metals per se, and do not shed any light on mining methods or on cyanidation vs. other types of milling/recovery processes for extraction of the precious metals from the ores. They also cover only industrial demand for gold and silver. As stated earlier, this demand has only minor influence on the domestic price of these commodities.

### 2.2.3 Estimated Total Potential Cyanide Present in Mining Wastes

Estimates of the total volume of existing cyanide-containing spent ores are not available. The "mill tailings" reported by Coppa (1984) include cyanidation, but other processes as well. Another estimation approach would be based on the amount of cyanide used, but these data are not available from DuPont. While many sources (Intermountain Soils Inc. 1985, Chamberlain and Pojar 1984, Clem 1982, McClelland and Eisele 1982, Heinen et al. 1978) report the cyanide solutions used for leaching on the basis of pounds of cyanide per ton of aqueous solution (i.e., about 1 lb cyanide/1 ton water), some sources (De Vries, personal communication, White 1977, Scott and Ingles 1981) report cyanide leaching solutions as approximately 1 lb cyanide per 1 ton ore. This solution rate apparently takes into account the extraction of precious metals, the ore grade and its impurities, as well as the recycling of the barren solution, resulting in a rate of consumption by spent ore of 1 lb cyanide per 1 ton ore. Therefore, based on these assumptions, every ton of spent ore generated by cyanidation leaching contains an upper limit of approximately 1 lb of cyanide, in some combination of free cyanide and metallo-cyanide complexes; the combination of free and complexed cyanide is defined as being total cyanide. Not all the complexes will be strongly bound, stable complexes; some will be moderately strong or weak complexes which may dissociate with time, although the fate of the free cyanide liberated from complexed cyanides is apparently not accounted for in the above estimates.

Presumably some (most?) of the free cyanide liberated will be released to the atmosphere, providing that the pH values in the heaps and tailings ponds are not highly alkaline. If the pH values remain above 9, the free cyanide ion will remain in solution and might percolate into the ground water or run off into surface water. Returning to the assumption that cyanide leaching results in an ultimate consumption of 1 lb cyanide/1 ton ore, Table 2-4 shows that there were about 18 million metric tons of gold ore treated by heap leaching during 1984; thus, by heap leaching alone in 1984, almost 20 million pounds of total cyanide were sprayed on heap leach gold ore. This gross estimate is an upper limit for the amount of residual cyanide remaining in cyanide-bearing spent heap leach gold ores, and does not include vat tailings from gold processing or either heap-leaching or vat processing of silver ores. Nor does the estimate take into account any treatment or washing of the spent ore or dissociation, degradation, or volatilization of the cyanide-bearing wastes.

The total volume of cyanidation waste ores generated by recovery of gold and silver in 1984 cannot be determined based on the available data from the Bureau of Mines. Some ores are treated to recover both gold and silver, so they appear in tabulations for both precious metals, thus total ore generated cannot be obtained by addition. Some of the residual cyanides are removed as liquid wastes and some lost to the atmosphere as hydrogen cyanide gas. In addition, the total quantity of "mill tailings" generated since 1910, 300 million short tons as reported by Coppa (1984)

(Table 2-1), includes processes other than cyanidation; therefore, only some unknown portion of ore volumes contains the estimated 1 lb cyanide/1 ton ore. Thus, with the available data, it does not appear to be possible to estimate the total cyanide potentially present in mining wastes.

### 2.2.4 Quantification of Concentrations of Cyanide in Various Types of Wastes

Heap-leaching operations for precious metal recoveries are growing more rapidly than vat extraction, in terms of rates of the increases in both ore treated and gold and silver recovered (Table 2-4). Every year since 1981, there has been more ore treated by heap leaching than by vat extraction, according to the Minerals Yearbook (Lucas 1985a, Reese 1985a). However, there is considerably less information available on cyanide concentrations in spent ores from heap leaching than from waste tailings resulting from vat extraction. Heap-leaching has become prominent only in the last few years, accounting somewhat for the limited historical data base. In addition, heap material is more heterogeneous, has a wider range of size distributions, and therefore is more difficult to sample and analyze for cyanide concentration, compared with vat tailings.

Data available for cyanide concentrations in waste ore exhibit variability because of differences in the ores themselves and the types of metallo-cyanide complexes that will form. The dissociation of the metal complexes may result in the formation of other, different metallo-cyanide complexes or, more importantly, liberation of free cyanide which, depending on the pH, may form hydrogen cyanide which may volatilize.

USEPA (1976) reported that free cyanide concentrations in the range from 0.05 to 0.10 mg/l (as cyanide) have proved eventually fatal to many sensitive fishes, and free cyanide levels above 0.2 mg/l probably are rapidly fatal to most fish species. It was concluded that since cyanide concentrations as low as 0.01 mg/l have been reported to cause adverse effects of fish, an ambient concentration of 0.005 mg/l was set as the criterion level to provide protection for freshwater and marine aquatic life and wildlife.

USEPA (1976) reviewed the toxic action of the free cyanide, an inhibition of the oxygen metabolism and blockage of the oxygen exchange in tissues. The conversion of free cyanide to thiocyanate (SCN) was considered to be the primary method of detoxification of cyanide, but Heming and Thurston (1985) reported results of studies which suggested that excited fish are more sensitive than had been previously reported.

Heming and Thurston (1985) also reported that both ferrocyanide and ferricyanide were more acutely toxic to rainbow trout when tested under light than when tested in total darkness. The reason is because iron cyanides are very stable but exhibit the phenomenon of photodecomposition. The stability of other metallo-cyanide complexes is variable, with some being readily dissociated to free cyanide and others being extremely stable.

USEPA (1983) reported that the toxicity to aquatic organisms of most simple cyanides and metallocyanide complexes is due mainly to the presence of HCN derived from dissociation, photodecomposition, and hydrolysis of the cyanide-containing compounds. The cyanide ion ($CN^-$) was also reported to be toxic, but most metallo-cyanide complexes have relatively low toxicity. Thus, the important form in terms of concentration measurement within cyanide-bearing wastes as well as release from these wastes is free cyanide in the hydrogen cyanide form, but it is also important to measure the concentration of the total cyanides because of their potential for degradation and formation of free cyanides. (Section 2.3.1 describes the difficulty in determining the concentrations of individual metallo-cyanide complexes, and formation-dissociation kinetics of the complexes which, together with free cyanides, are analyzed and reported as the total cyanide concentration.)

(1) Cyanide concentrations in spent heap leach ore. Engelhardt (1985) and Milligan (1985a) both reported the effects of natural degradation of cyanide at a recently-terminated heap leach operation (see Section 2.3.3.1 for details of the study design). At three months after termination of the heap leaching, free cyanide concentrations in 11 core samples within the heap ranged from 7.7 mg/kg to 196.2 mg/kg (Table 2-6). Fifteen months later, free cyanide concentrations in the 11 core sampling locations ranged from <6.8 mg/kg to 37.5 mg/kg. It was reported that the concentration would be "less than 1.0 mg/kg" within four years after termination of leaching, but this is based on an extrapolation of relatively few data points. Free cyanide concentration levels were determined by agitating the cored sample of spent ore for one hour with distilled water, filtering, and analyzing the filtrate.

Ray (1985) reported total cyanide concentration data for analyses of various heaps in the southeastern desert of California (Table 2-7). Total cyanide levels were found to be highly dependent upon the mineral composition of the ore; some metallo-cyanide complexes are very resistant to natural degradation, and total cyanide levels were found to be persistent within the heap materials containing these complexes. The method of total cyanide analysis involved a 24-hour leaching in the dark using a 1.25 N NaOH solution, filtration, analysis of the filtrate by the EPA (1979) distillation/destruction method, and colorimetric measurement.

ERCO (1984) used the EPA Office of Solid Waste (1982) method to analyze total cyanide and cyanide amenable to chlorination. A sample

38

Table 2-6. Free Cyanide Concentrations in Eleven Locations in the Darwin Heap

| Darwin ID No. | Heap No. | Percent moisture | | Free cyanide (mg/kg) | | Percent loss of free cyanide during 15 months |
|---|---|---|---|---|---|---|
| | | Jan 83 | Mar 84 | Jan 83 | Mar 84 | |
| Q3S2 | 1 | 14.6 | 14.6 | 102.6 | <6.8 | 93.4 |
| Q3S3 | 2 | 14.0 | 13.0 | 118.8 | 13.4 | 88.7 |
| Q3S4 | 3 | 16.4 | 15.5 | 196.2 | 23.8 | 87.9 |
| Q6S1 | 4 | 14.7 | 14.6 | 144.8 | 22.2 | 84.7 |
| Q6S2 | 5 | 14.6 | 12.5 | 87.2 | 20.0 | 77.1 |
| Q6S3 | 6 | 15.9 | 14.3 | 155.0 | 28.4 | 81.7 |
| Q6S4 | 7 | 15.2 | 12.0 | 91.4 | <6.8 | 92.6 |
| Q9S1 | 8 | 14.3 | 12.2 | 146.8 | 37.5 | 74.5 |
| Q9S2 | 9 | 14.8 | 11.9 | 34.7 | <6.8 | 80.4 |
| Q9S3 | 10 | 14.5 | 11.8 | 8.5 | <6.8 | 21.2 |
| Q9S4 | 11 | 13.4 | 11.4 | 7.7 | <6.8 | 16.9 |

Source: Engelhardt (1985).

Table 2-7. Total Cyanide Concentrations for Various Heap Leach Operations in California

| Description of ore samples | Run # | mg/kg |
|---|---|---|
| Samples low in iron | 1 | 0.97 |
| | 2 | 0.41 |
| | 3 | 0.24 |
| | 4 | 0.42 |
| | 5 | 0.12 |
| | 6 | 0.27 |
| | 7 | 1.5 |
| | 8 | 0.90 |
| Samples high in iron and copper | 9 | 75 |
| | 10 | 34 |
| | 11 | 9.0 |
| Samples high in iron, mined for silver | 12 | 17.1 |
| | 13 | 5.9 |
| | 14 | 11.2 |
| | 15 | 105 |
| Samples high in copper | 16 | 41 |
| | 17 | 83 |
| | 18 | 91 |
| | 19 | 5.7 |
| Samples low in cyanicides | 20 | 0.82 |
| | 21 | <0.05 |
| | 22 | <0.05 |
| | 23 | <0.05 |
| | 24 | 1.0 |
| | 25 | 0.07 |
| | 26 | <0.05 |
| | 27 | 0.12 |
| | 28 | 0.20 |
| | 28 | 0.20 |
| | 29 | <0.05 |
| | 30 | <0.05 |

Source: Ray (1985).

collected from leached ore at the Zortman and Landusky heap in Montana was reported to have a concentration of 4.5 ug/g for both total cyanide and cyanide amenable to chlorination. Concentrations of both parameters were reported to be <2 ug/g for inactive heap leach material from the Pinson Mine in Nevada.

John Pahlman of the U.S. Bureau of Mines (1986) provided a study on sampling and analysis of old heap wastes at Tombstone Silver Mines, Inc. (Arizona). · The spent heap leach wastes from previously extracted ores were sampled and analyzed for cyanide. Levels of cyanide ranged from "nil" (less than detectable) to 0.40 mg/l; most of the values were <0.1 mg/l. The method of analysis appears to have relied on extraction of the samples (75 g) with 150 ml of water and 0.1 g of lime (CaO) for one hour. Using an assay method from the U.S. Bureau of Mines, however, in which extraction was carried out for approximately 12 hours on 40 g of ore with 200 ml of water and 1 g of sodium hydroxide, cyanide values were obtained that were two to ten times greater, with more than half the values below the detection limit of 0.25 mg/kg, and the detectable values ranging from 0.35 to 0.86 mg/kg.

James M. Montgomery, Consulting Engineers, Inc. (1986) described free cyanide analyses of waste ore from a stibnite (antimony ore) mining operation in Idaho. After cyanidation extraction, the ore had been treated with an aqueous chlorine solution, mechanically spread out, and exposed to the atmosphere. The average 10-day decrease in cyanide level was approximately 50 percent of the concentration level sample collected on the first day.

James M. Montgomery (1986) also reported on analyses of samples from a South Dakota gold heap leach operation, which was presumably treated with an aqueous chlorine solution at closure. Analyses showed free cyanide concentrations in the spent ore ranging from 0.06 to 0.18 mg/l.

Monitoring of effluent from the overflow pond showed a maximum free cyanide concentration of 0.058 mg/l during a two-year period. This pond received all the overflow runoff from the treated leach heap.

McGrew (1985) described monitoring of cyanide concentrations from the Annie Creek leach heap operated by Wharf Resources in South Dakota. Leach heaps were deactivated in 1982 by running a hypochlorite solution through the heap and subsequently water had been pumped through the heaps. Cyanide concentrations have been monitored in the runoff water. In the first month of water recirculation, there was more than a 10-fold decrease in both total cyanide and Method-C cyanide (total cyanide decreased from 300 ppm to 3.4 ppm, and Method-C cyanide decreased from 300 ppm to 10 ppm). After a year, the cyanide concentration apparently continued to decrease. Values for cyanide from December 1983 to June 1985 ranged from 0.2 to 0.01 mg/l for Method-C cyanide.

McGrew (1985) also described an autopsy of the Annie Creek test heaps (called "tailings" in the report) following neutralization by water recirculation. In the autopsy, a backhoe was used to excavate test pits 6-feet square and 4- to 6-feet deep in various locations on the test heaps. Of the 30 "tailings" samples analyzed for total cyanide at depth intervals of 1 foot, 21 samples indicated total cyanide concentrations to be less than the detection limit of 0.5 ppm, five analyses were between 0.5 and 0.6 ppm, three were between 0.6 and 0.7 ppm, and one was higher than 0.7 ppm (0.98 ppm in a 0 to 2 foot-deep sample). Of the 30 samples analyzed for Method C-cyanide, 28 were below the detection limit of 0.5 ppm, and the other two were between 0.5 and 0.6 ppm. The study also included analyses of clay samples of the bentonite and/or the natural clay that comprised the heap pad panel linings. Of the 23 samples analyzed at 2-inch depth intervals for total cyanide and Method C-cyanide, none of the samples showed cyanide penetration below a depth of 4 inches. The only detectable Method C-cyanide concentration was 0.83 ppm in a 2- to 4-inch sample; of the 23 total cyanide concentrations, only five showed detectable levels (0.5 ppm), ranging from 1.29 to 3.92 ppm in the 0- to 2-inch and 2- to 4-inch clay samples.

Ambient air monitoring in the vicinity of the Annie Creek leach heap operated by Wharf Resources was also reported (Stampfli 1986). The data were collected at various locations from 10 m to 100 m from the heap. Concentrations ranged from less than 2 $u/m^3$ to 259 $u/m^3$, with all but 4 of the 45 samples being less than 92 $u/m^3$. The data reported appeared to indicate that (1) atmospheric cyanide levels decline with an increase in wind speeds, and (2) downwind cyanide levels decrease inversely with distance from the heap source.

Two tests were also conducted to determine transport for cyanide in natural soils that were characteristic of the mining area at the Annie Creek heap leach (Wharf 1982). The results indicated that after a brief lag period of a few days, the cyanide levels in the effluents from packed soil columns had decreased by natural biological processes to less than half of the concentration of the originally applied solutions, and that further reductions in cyanide concentration continued over the next six weeks (Table 2-8).

(2) Cyanide concentrations in tailings from vat leaching operations. Hendrix et al. (1985) reported that mill tailings at two sites in Nevada had been sampled and that analysis methods were developed for determining total and free cyanide concentrations. Tailings collected from a depth of 3 meters at one of the sites showed total cyanide concentrations of 3.75 to 5.6 ppm and free cyanide concentrations of 1.0 to 1.16 ppm, based on replicate analyses. Further sampling and analyses at these and other sites (total of six tailings ponds) have been performed.

Table 2-8 Results of Tests with Cyanide Solutions (in ppm)[a] Added to Columns Containing Native Soil from the Area of Annie Creek Mine, SD

| Test conditions | Test 4-SS (Nominally 150 ppm) Date | Free CN | Total CN | Test 5-SS (Nominally 1 ppm) Date | Free CN | Total CN |
|---|---|---|---|---|---|---|
| Influent solution | 8/16 - 8/19/82 | 36.5 | 149 | 8/25 - 8/27/82 | 1.0 | 1.0 |
| Effluent | 8/17 | 4.5 | 65 | 8/26 | <0.01 | 0.03 |
| Effluent | 8/18 | 17 | 46.5 | 8/27 | <0.01 | <0.01 |
| Effluent following fresh-water flush | 10/4 | 2.4 | 29 | 10/4 | <0.05 | <0.05 |

Source: Wharf (1982).

[a] Cyanide solutions added to soil columns at about 0.5 gal/min/ft$^2$ for 3 days.

Dr. J. L. Hendrix, University of Nevada - Reno, submitted a quarterly report to the Bureau of Mines (1985). Samples were analyzed for total and free cyanide from a vat tailings pond both one month and three months after the pond was filled. Levels of cyanide in comparable samples are given in Table 2-9. Other locations in the pond sampled one month after closure showed a free cyanide concentration range from 1.50 to 12.85 ppm, and a total cyanide range from 3.03 to 24.95 ppm. Several observations are apparent: (1) the tailings pond is not homogeneous in levels of total or free cyanide; (2) there is neither a constant increase nor decrease in cyanide levels from the surface to the lowest sampling depth; and (3) comparisons of one- and three-month samples from the same sites indicate that there are differences not only in the rates of degradation of complexed cyanide to free cyanide, but also in the losses of free cyanide among the various sampling sites.

Hendrix (1985) also determined the cyanide levels in a vat tailings pond that was more than ten years old. In a telephone conversation on May 16, 1986, with Dr. Bentley Gregg (Versar), Hendrix stated that the pH of some samples from this pond were as low as pH 4. The highest concentrations of free cyanide were found in the samples of greatest acidity (lowest pH). The reported total cyanide levels in this pond ranged from "zero" to 36.42 ppm; free cyanide levels ranged from "zero" to 4.94 ppm.

Simovic (1984) and Simovic et al. (1985) reported that a tailings pond wastewater collected from Cullaton Lake Mine in the Northwest Territories had been tested in a continuous stirred tank reactor (CSTR); the initial concentration of 22.3 mg/l decreased after 1, 3, 7, and 30 days to 17.2 mg/l, 12.7 mg/l, 8.9 mg/l, and 3.9 mg/l, respectively.

Schmidt et al. (1981a, b) reported data for the tailings pond at Dome Mines Limited near Timmins, Ontario. The tailings pond had a 70-hour

Table 2-9 Cyanide Levels (ppm) in a Vat Tailings Pond Sampled One and Three Months After Closure

| One month | L-1 | | L-2 | | L-3 | |
|---|---|---|---|---|---|---|
| Depth (meter) | Total | Free | Total | Free | Total | Free |
| Surface | 17.55 | 4.59 | 8.01 | 4.97 | 10.08 | 4.20 |
| Surface | 14.85 | 5.67 | 9.66 | 4.69 | 8.10 | 4.20 |
| 1 | 9.86 | 3.95 | 10.16 | 4.36 | 11.40 | 2.48 |
| 1 | 9.37 | 4.19 | 10.16 | 4.36 | 11.40 | 2.48 |
| 2 | 6.24 | 3.74 | 3.28 | 1.26 | | |
| 2 | 6.24 | 3.74 | 2.72 | 2.02 | | |

| Three Months | L-1 | | L-2 | | L-3 | |
|---|---|---|---|---|---|---|
| Depth (Meter) | Total | Free | Total | Free | Total | Free |
| Surface | 18.81 | 4.15 | 6.98 | 0.00 | 8.36 | 1.11 |
| Surface | 19.64 | 3.60 | 6.38 | 0.00 | 8.36 | 1.11 |
| 1 | 2.92 | 2.92 | 0.00 | 0.00 | 9.77 | 1.47 |
| 1 | 2.92 | 2.92 | 0.00 | 0.00 | 9.77 | 1.71 |
| 2 | 1.18 | 1.18 | 1.5 | 1.5 | 3.23 | 1.49 |
| 2 | 1.18 | 1.18 | 1.5 | 1.0 | 3.23 | 1.49 |
| 3 | 8.82 | 0.76 | 1.8 | 1.03 | 3.97 | 1.99 |
| 3 | 9.07 | 1.01 | 1.8 | 1.03 | 3.72 | 1.99 |

Source: Hendrix (1985)

mean residence time, and the influent and effluent wastewaters were sampled frequently over a 61-week period (Table 2-10). Average total cyanide removal during waste water passage through the pond was 65 percent. Effluent cyanate (CNO) concentrations increased during the warmer months while the total cyanide, cyanide amenable to chlorination, and thiocyanate (CNS) concentrations decreased, suggesting that oxidation was occurring within the pond.

Fox (1984) reported analyses of total cyanide and various metals in gold mill tailings in the Black Hills of South Dakota. Maitland (74-year-old deposits) and Homestake (5-year-old deposits) showed total cyanide concentrations of 0.71 mg/kg and 0.03 mg/kg, respectively. The Wasp tailings deposit was 90 years old and had a reported concentration of 3.35 mg/kg. The study did not describe the cyanidation processes used for the Wasp tailings or specify the minerology of the tailings, but the data suggest that the cyanides in the 90-year-old tailings have been persistent and may be chemically bound or sorbed to the tailings. The aqueous concentration of total cyanide was <0.03 mg/l in surface waters both adjacent to the Wasp tailings deposit and 91.4 meters downstream. The EP Toxicity leachate value for total cyanide in the Wasp tailings was <0.05 mg/l as might be expected since the analysis procedure involves an extended acidic (pH 5) extraction in an open container.

ERCO (1984) sampled the Pinson Mining Co. and the Hecla Mining Co. gold vat leaching facilities (Table 2-11). At the Hecla Mine some of the cyanide in the fresh tailings and most in the tailings pond settled solids were firmly complexed cyanide, that is cyanide not amenable to chlorination (i.e., possibly ferrous- or ferric-cyanide complexes). Cyanide analyses were not performed for mining materials collected from the gold operation at Standard Metals Corp., Silverton, Colorado, nor from two silver operations, at Sunshine Mining Co., Kellogg, Idaho and Asarco Inc., Troy, Montana. Cyanide analyses were reported for mining

Table 2-10. Tailings Pond Influent and Effluent Concentrations at Dome Mines Limited, Timmins, Ontario[a]

| Constituent | Concentration (mg/l) Influent | Concentration (mg/l) Effluent |
|---|---|---|
| Total cyanide | 18.2 | 6.9 |
| Cyanide amenable to chlorination | 17.9 | 6.3 |
| Cyanate (CNO) | 2.4 | 4.0 |
| Thiocyanate (CNS) | 11.5 | 9.1 |

Source: Schmidt (1981a, b)

[a] Average of composite samples from September 9, 1979 to November 15, 1980.

Table 2-11. Data from ERCO (1984) Mining Waste Study

| Sample type | Total cyanide | Cyanide amenable to chlorination |
|---|---|---|
| Pinson Mining Co.<br>Humbolt Co., Nevada | | |
| Fresh tailing | 130 ug/g | 130 ug/g |
| Pregnant heap leach liquor | 12 mg/l | 12 mg/l |
| Hecla Mining Co.<br>Ferry Co., Washington | | |
| Fresh tailings | 40 ug/g | 30 ug/g |
| Tailing pond settled solids | 16 ug/g | 2.2 ug/g |
| Tailing pond liquid | 15 mg/l | 15 mg/l |
| Amax Lead Co.<br>Boss, Missouri | | |
| Tailings pond liquid | -- | 0.025 mg/l |
| Cyprus Badgad Copper<br>Badgad, Arizona | | |
| Liquid from tailing pond | 3.2 mg/l | 3.2 mg/l |
| Liquid from seepage collection pond | 1.3 mg/l | 1.3 mg/l |
| Inspiration Consol.<br>Inspiration, Arizona | | |
| Dump leach liquors | 0.011 mg/l | 0.011 mg/l |
| Cities Service Co.<br>Copperhill, Tennessee | | |
| Liquid from tailing pond | 0.57 mg/l | 0.57 mg/l |

waste materials collected from the following non-precious metal facilities: Amax Lead Co., Boss, Missouri; Cyprus Bagdad Copper Co., Bagdad, Arizona; Inspiration Consolidated Copper, Inspiration, Arizona; Phelps Dodge Copper (Copper), Tyrone, New Mexico; and Cities Service Company (Copper), Copperhill, Tennessee. Concentrations were less than detectable in all types of materials sampled, except for the low concentrations reported for the materials indicated in Table 2-11.

PEI (1983) also sampled various mining wastes materials. Three different laboratories performed analyses on replicate samples, thus there are ranges of concentrations reported in Table 2-12. In addition, two sets of settled solids data were reported (WS-116-CP and WS-116-CT, which are shown in Table 2-12 as "settled solids #1" and "#2", respectively); the differences, if any exist, between the types of analyses conducted on the two sets of settled solids data were not indicated. Based on the samples reported from the two gold mines, it is clear that there was considerable variability among the various laboratories; for settled solids, one of the laboratories showed significant within-laboratory variability. In general, most of the samples analyzed in this PEI data set showed concentrations of cyanide amenable to chlorination very close to the total cyanide concentrations, indicating that little of the total cyanide was present as firmly-bound, difficult-to-dissociate cyanide; thus, presumably only low concentrations of recalcitrant metallo-cyanide complexes were present.

Scott and Ingles (1981) presented cyanide concentration data for gold mill tailings effluents being discharged as wastes at various Canadian facilities (Table 2-13). Based on the two-hundred-fold difference between the low and high total cyanide concentration, it is difficult to generalize about the total cyanide concentrations in Canadian gold mill tailing effluents.

Table 2-12. Data from PEI (1983) Mining Waste Study

| Sample type | Total cyanide | Cyanide amenable to chlorination |
|---|---|---|
| Newmont's Carlin Gold Mine<br>Carlin, Nevada | | |
| Fresh tailings | 3.1 - 61 mg/l | 3.1 - 85 mg/l |
| Settled solids - # 1 | 2.12 - 192 ug/g | 0.44 - 191 ug/g |
| - # 2 | 4.20 - 36 ug/g | 3.29 - 24 ug/g |
| Liquid fraction | 60.70 - 76.5 mg/l | 60.7 - 76.3 mg/l |
| Homestake's Gold Mine<br>Lead, South Dakota | | |
| Fresh tailings | 0.78 - 11 mg/l | 0 - 8 mg/l |
| | 217 - 866 ug/g | 169.8 - 844 ug/g |
| Settled solids - # 1 | 1.56 - 71.4 ug/g | 0 - 63.8 ug/g |
| - # 2 | 2.28 - 15 ug/g | -- |
| Liquid fraction | 12 - 80 mg/l | 6.9 - 77.8 mg/l |
| Duval's Sierrita Mine<br>Tucson, Arizona | | |
| Fresh tailings | 0.26 - 0.79 mg/l | 0 - 0.14 mg/l |
| Settled solids - # 1 | 0.07 - 1.7 ug/g | 0 - 1.7 ug/g |
| - # 2 | <0.06 - 0.09 ug/g | 0 - 0.01 ug/g |
| Liquid fraction | <0.02 mg/l | 0 mg/l |
| St. Joe's Viburnum Lead Mine<br>Viburnum, Missouri | | |
| Fresh tailings | <0.025 - 0.004 mg/l | 0 |
| Settled solids - # 1 | <0.01 - <1 ug/g | 0 |
| - # 2 | <0.01 - 0.03 ug/g | |
| Climax Molybdenum's Co.<br>Henderson Mine. | | |
| Fresh tailings | 0.24 - 0.79 mg/l | 0 - 0.214 mg/l |
| Settled solids - # 1 | 0.20 - 0.236 ug/g | 0.094 - 0.14 ug/g |
| - # 2 | <1 - 0.15 ug/g | <1 - 0.04 ug/g |
| Liquid fraction | <0.02 - 0.179 mg/l | <0.02 - 0.15 mg/l |

Table 2-13. Effluent Concentrations (mg/l) for Some Typical Canadian Gold Mill Tailings, as Reported by Scott (1985)

| Total cyanide | $CN_w$[a] |
|---|---|
| 0.30 | |
| 0.87 | 0.42 |
| 1.2 | |
| 2.8 | 0.34 |
| 3.3 | 3.1 |
| 4.8 | 4.5 |
| 6.8 | |
| 13.0 | |
| 21.0 | 16.2 |
| 25.0 | 18.6 |
| 33.0 | |
| 61.0 | 42.0 |

[a] $CN_w$ - Weak acid dissociable cyanide by ASTM Method-C, i.e., cyanides less stable than iron cyanide.

J. C. Sprague (1986), Mine Manager of Barrick Mercur Gold Mines, Inc., reported on recent analyses of weak-acid dissociable cyanide concentrations in 80-year old gold mill tailings. A total of 33 samples were taken at 5-foot intervals from four drill holes (30, 90, 120, and 120 ft. in depth) in gold mill tailings that were emplaced during 1892 to 1908. The samples analyzed were from the alternate depth intervals (i.e., at the 10-foot intervals) and were analyzed by ASTM Procedure D2036-82 Method C (Weak-Acid Dissociable-C or WAD-C). The reported cyanide levels ranged from 0.30 to 1.80 ppm (although the memo reported that the range was 0.40 to 1.70 ppm). The lower levels of cyanide were in samples from the surface of the tailings, as would be expected because of volatilization and leaching of free cyanide. Analysis for gold showed greater concentrations at the lower depths of the tailings and in the alluvium base, suggesting that leaching in situ had taken place since emplacement of the tailings.

The continuing but slow transport of gold in these old Mercur Mill tailings is due to the continued presence of free cyanide in the tailings and the aqueous solubility of the anionic gold-cyanide complex. Although free cyanide is being volatilized and/or leached from the tailings, small additional amounts are being constantly generated by the decomposition of sparingly soluble metallocyanide complexes that have remained within the wastes from the vat extraction. This newly formed free cyanide is then available to complex with residual gold and mobilize it for transport in the direction of percolating rainwater.

Sprague (1986) reported that initial treatment of samples according to Method C involves leaching with 1.25 N sodium hydroxide. The leachate is then acidified with acetic acid to pH 4-5 for distillation and subsequent titration of hydrogen cyanide. Elimination of both the acidification step (with acetic acid) and the distillation step yielded identical cyanide concentrations. However, extraction with water rather than 1.25 N sodium hydroxide decreased the amount of cyanide released from the samples to 30 percent of that which had been released by sodium hydroxide. This means that dissociation of metallocyanide complexes in the sample occurs during extraction with strong base, and the name attached to Method C, i.e., Weak-Acid Dissociable, is a misnomer.

An anonymous study was provided by DuPont (DeVries 1986) describing the monitoring of a tailings pond located in Western Australia (Table 2-14). The main point to be derived from the monitoring data is that free cyanide decreased during passage through the system and the residual cyanide present in the tailing pond was mostly the very stable metallocyanide complexes. Another significant factor in the removal of cyanide from this pond was the conversion of cyanide to thiocyanate, indicating that metal sulfides were apparently present.

(3) Cyanide concentrations in barren bleed ponds. Simovic et al. (1985) reported the initial total cyanide concentration was 145 mg/l in the barren bleed pond of an unspecified Canadian gold mill (possibly Cullaton Lake Mine in the Northwest Territories). The concentration in the barren bleed pond had decreased by natural degradation to 2.3 mg/l after a retention time of 55 days.

Schmidt et al. (1981a, b) reported that the initial total cyanide concentration was 68.7 mg/l in the barren bleed-holding pond at Dome Mines Limited near Timmins, Ontario. By the time the effluent was discharged about five and a half months later, the concentration had decreased by natural degradation to 0.08 mg/l (see Section 2.3.3.2 for further discussion of this site). Barren bleed solution was also subjected to batch test alkaline chlorination studies to assess the treatability of the Dome Mine wastewaters, and the total cyanide concentration decreased from 63.0 mg/l to 0.4 mg/l in 150 minutes.

Table 2-14 Cyanide Concentrations (in ppm) in a Carbon-in-Pulp (CIP) Cyanide Mill Tailings Pond in Western Australia

| | CIP plant tailings[a] | Tailings slurry discharged into tailings pond[b] | Tailings pond supernatant[c] |
|---|---|---|---|
| Free CN ($CN_f$): | | | |
| October 24, 1983 | 245 | 120 | 12 |
| November 3, 1983 | 1,000 | 120 | 42 |
| Total CN ($CN_t$): | | | |
| October 24, 1983 | 295 | 217 | 214 |
| November 3, 1983 | 1,050 | 485 | 497 |
| CN as complexes ($CN_t - CN_f$): | | | |
| October 24, 1983 | 50 | 97 | 202 |
| November 3, 1983 | 50 | 365 | 455 |
| Thiocyanate: | | | |
| November 3, 1983 | 82 | 78 | 196 |

Source: Anonymous (provided by DeVries 1986).

[a] 44 percent solids; combined oxide ore plus gold float tails after 18 hour cyanidation, along with calcine after 72 hour cyanidation, taken after adsorption circuit.

[b] Mixture of CIP tailings and nickel tailings thickener underflow at 55 percent solids, pumped about 1.5 km to the tailings pond.

[c] Clear solution; no water is discharged from the pond, with water losses attributed to evaporation "and likely a small amount of seepage year round."

ERCO (1984) reported analyses of the "barren pond, leach liquor" at the Zortman and Landusky heap-leaching operation in Montana; both the total cyanide and the cyanide amenable to chlorination concentrations were reported to be 270 mg/l.

Scott and Ingles (1981) presented cyanide concentration data for barren bleed solutions for various Canadian gold mills (Table 2-15). Reported concentrations for influent solutions to barren bleed ponds, in general, appear to be much higher than the cyanide concentrations in the effluents to mill tailings ponds.

### 2.2.5 Conclusions

The data reviewed indicate that there have been substantial increases in the practice of cyanidation of precious metal ores in recent years. The ore grades of vat leached ores have increased and heap leach ore grades have decreased. The volumes of gold ore and silver ore treated with cyanide have increased, but ore volume data are available from the Bureau of Mines only for the last decade. Moreover, the data are reported separately for gold and silver leaching, but there is overlap in the ores processed, so the total volume of precious metal ores treated by cyanidation cannot determined.*

The data on concentration levels in cyanide-bearing wastes are limited and there is considerable varability in the available data. Because there are different cyanidation practices and because different ores have a variety of mineral characteristics, it is expected that the cyanide concentrations will vary widely. A more complete data base would allow a better assessment of the residual cyanide in waste materials which, in turn, would provide a better indication of the amount of cyanide available for potential release.

---

*Personal communication with Jean Moore, Bureau of Mines, Washington, D.C.

Table 2-15. Concentrations (mg/l) of Cyanides in Some Typical Canadian Gold Mill Barren Bleed Solutions, as Reported by Scott (1985)

| Total cyanide | $CN_w$ [a] | Thiocyanate (CNS) |
|---|---|---|
| 74 | | 50 |
| 86 | | 42 |
| 220 | | 180 |
| 300 | | 54 |
| 310 | | |
| 310 | 220 | 330 |
| 400 | | |
| 400 | | 113 |
| 450 | | |
| 610 | | 400 |
| 890 | | |
| 1,000 | 710 | 1,900 |
| 2,000 | 1,900 | 1,100 |

[a] $CN_w$ - Weak acid dissociable cyanide by ASTM Method-C, i.e., cyanides less stable than iron cyanide.

The data available on changes in cyanide concentration in waste materials over time are very limited. One heap leach operation and one vat leach operation were each sampled on two dates, but the rate of degradation cannot be determined with certainty because of the variability in free cyanide concentrations among the sampling depths and locations. Tailings pond data are available for various Canadian mills, but the variability in concentration data, ore compositions, and cyanidation practices between U.S. and Canadian mills may limit the usefulness of any direct observations concerning the data base.

## 2.3 Environmental Fate, Releases, and Transport of Cyanides

### 2.3.1 Assessment of Data on the Potential for Cyanide Releases

One of the objectives of this task has been to review the literature available on vat extraction and heap leaching, especially information on any releases of cyanide. Various review reports were examined for any information available on reported releases and, in addition, numerous journal articles were reviewed on individual sites to determine whether any releases had been documented. It is clear from this review of the literature that every site is unique, that process configurations of the site and meteorological conditions differ from site to site, and that generalizations about all sites based on observations at only a few sites would not be representative.

In quantifying the cyanide content and potential for releases from spent heap leach ores, vat mill tailings, and barren bleed solutions, it is important to know the concentrations of both free cyanide and metallo-cyanide complexes, the combination of which are measured as total cyanide. It is also important to quantify the mineral content of the specific ore body. Using atomic absorption spectrophotometery or inductively coupled plasma analysis will only measure the amounts of the metals themselves. These methods will not determine the specific concentrations of the metallo-cyanide complexes or the ore minerology, and new methods will be required for these determinations.[*] The formation kinetics of the various complexes determine the initial total cyanide content of the cyanide-bearing wastes, and the dissociation kinetics of the complexes determine their degradation and the formation of free cyanides. When the metallo-cyanide complexes dissociate, the free cyanides formed have the potential to migrate within the waste and be released. Under highly alkaline conditions (pH greater than 9), the cyanide ion will predominate and aqueous release and transport is possible. At pH of 9 or less, the hydrogen cyanide form will predominate. This form is volatile, so atmospheric release is a likely route of loss from the cyanide-bearing wastes at pH of less than about 9. ERCO (1984) reported that the pH of the leached ore at Zortman-Landusky in Montana was 8.3, and the inactive heap leach material at Pinson Mining in Nevada was 8.8. Depending on the pore spaces and potential for escape of volatile gases, these pH values suggest that escape of hydrogen cyanide gas may be a loss mechanism from spent heap leach ore. Simovic et al. (1985) have stated that vat tailings have pH of 8.1 to 8.2 and that volatilization of cyanide from these tailings is an "important loss mechanism".

The types of ores treated by cyanidation are important, because some types of ores contain metals that form insoluble, stable metallo-cyanide complexes (that is, do not readily leach or dissociate) (Table 2-16). Because of the presence of these metals which form strong complexes, the total cyanide levels may remain high in the spent ores at some sites. In addition, the conditions that could result in dissociation of these complexes are poorly described; for example, it is unclear what effect

---

[*] Dr. J.L. Hendrix, University of Nevada-Reno, indicated in a personal communication that he was developing methods to determine the amounts of each of the metal species of metallo-cyanide complex present.

Table 2-16. Relative Stability of Cyanide Complexes

| Terms | Forms of cyanide |
|---|---|
| 1. Free cyanide | $CN^-$, HCN |
| 2. Simple compounds | |
| a) readily soluble | NaCN, KCN, $Ca(CN)_2$, $Hg(CH)_2$ |
| b) relatively insoluble | $ZN(CN)_2$, $Cd(CN)_2$, CuCN,<br>$Ni(CN)_2$, AgCN |
| 3. Weak complexes | $ZN(CN)_4^{2-}$, $Cd(CN)_3^-$, $Cd(CN)_4^{2-}$ |
| 4. Moderately strong complexes | $Cu(CN)_2^-$, $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$, $Ag(CN)_2^-$ |
| 5. Strong complexes | $Fe(CN)_6^{4-}$, $Co(CN)_6^{4-}$, $Au(CN)_2^-$ |

Source: Scott and Ingles (1981).

would result from rainfall and the shifts in the pH balance of the interstitial moisture in the spent ore resulting from the atmospheric precipitation percolating into the spent ore.

Gold forms a very strong complex with cyanide; the binding of the complex is sufficiently strong that free (molecular) gold will be complexed (leached) from the ore during the cyanide leaching process and be solubilized as a gold and cyanide complex. This complexation also accounts for the extraction of silver during cyanidation, as well as the binding of other metals that the metallurgist would consider "impurities" in the ore body.

The affinity or tightness of the binding of the complex between the cyanide radical (the ligand) and the metal is quantified by means of a stability constant, based upon the mass action equilibrium between the metal ion and the ligand. Since more than one type of complex can form (i.e., there are various metals present in each ore), a cumulative or gross constant, $B_n$, is used to describe the reactions between the metals and cyanide:

$$M + n(CN) = M(CN)_n$$

The cumulative constant for individual metals can be determined by potentiometric titrations conducted both in the presence of and in the absence of the particular metal ion, with the titration results subjected to complex calculations usually performed by computer. In natural ore bodies with various metals present, these titrations would probably lead to more complicated endpoints.

The cumulative constant is presented as follows:

$$B_n = \frac{[M(CN)_n]}{[M][CN]^n}$$

C2

where the concentration units [ ] are expressed as moles per liter.

For the various metals found in different types of ore, cumulative constants for the individual metal ions are presented in Table 2-17. Milligan (1985b) assumed a ratio equal to $2 \times 10^{10}$ between the concentration of the cyanide-metal complex and the concentration of the metal, and solved the cumulative constant ($B_n$) equation to determine the free cyanide content [CN] necessary to form the cyanide-metal complexes in Table 2-17. Lead would require a free cyanide concentration of 1 mole per liter to achieve the assumed ratio of $2 \times 10^{10}$, while other metals would be dissolved and leach from the ore when mixed with smaller quantities of free cyanide.

Rather than existing as free metals in the ore, some of the metals in Table 2-17 may be present in the ore in the form of compounds more stable than the cyanide complex. This is favorable for cyanidation treatment for extraction of precious metals, because the presence of highly stable metal compounds may prevent the metal from dissolving in the sodium cyanide solution and consuming the cyanide, even in the presence of a high concentration of free cyanide in the leaching solution.

When the metals are not more strongly bound in other compounds and the surfaces of the metals are exposed to leaching solutions with the cyanide as the limiting reactant, the rate of metal dissolution by cyanide increases directly proportional to the free cyanide concentration present in the solution. This increased solubility of the metallo-cyanide complex with increases in the free cyanide concentration will hold up to the maximum dissolution rate of the metal-cyanide complex; beyond the maximum dissolution rate, further increases in the free cyanide concentration may have a slight retarding effect on the dissolution rate of the complex (Milligan 1985b).

Table 2-17. Cumulative Constants, $B_n$, for Various Metals Found in Precious Metal Ores

| Metal | Valence | n[a] | Log (10) of $B_n$ | Log (10) of [CN] |
|---|---|---|---|---|
| Cadmium | +2 | 4 | 16.85 | -1.6 |
| Cobalt | +2 | 6 | 19.09 | -1.5 |
| Cobalt | +3 | 6 | 64 | -9.0 |
| Copper | +1 | 4 | 27.3 | -4.3 |
| Gold | +1 | 2 | 47.5 | -18.6 |
| Gold | +3 | 4 | 56 | -11.4 |
| Lead | +2 | 4 | 10.3 | 0 |
| Mercury | +2 | 4 | 41.4 | -7.8 |
| Nickel | +2 | 4 | 31 | -5.2 |
| Silver | +1 | 4 | 21.1 | -2.7 |
| Zinc | +2 | 4 | 16.9 | -1.7 |

[a] n = number of cyanide molecules in the metallo-cyanide complex.

Source: Milligan (1985b).

As with most chemical reactions, the metallo-cyanide complex formation and dissolution of the metal, as well as the dissociation of the complex, are affected by temperature, because the activation energy requirement is temperature sensitive. Thus, the leaching rate of precious metals during colder conditions may be only 70 percent of the leaching rate during summer operating conditions (Milligan 1985b).

The dissociation of these metallo-cyanide complexes is also described by the equilibrium equation. As indicated in Table 2-16, some of the complexes are weak and free cyanide would be liberated. Some of this free cyanide may be available for binding with other metals to form more stable complexes, while other liberated free cyanide molecules may remain unbound and are available for transport through the waste materials and release to the environment. Thus, spent heap leach ores and vat mill tailings may be sources of long-term releases of cyanide, especially by volatilization of hydrogen cyanide, which is the dominant species of free cyanide at pH values of about 9 or less. These atmospheric releases would probably be at low concentrations.

Simovic et al. (1985) tested the dissociation rates by using four synthetic solutions of single metallo-cyanide complexes (Cu, Zn, Ni, and Fe). The synthetic solutions had initial total cyanide concentrations of 200 mg/l and were tested at pH 7 (phosphate buffer) at 4 °C and 20 °C. Tests were performed in 2-liter graduated cylinders that were aerated and illuminated with ultraviolet light. In all tests, there was an initial rapid decrease in the total cyanide concentrations (within the first 48 to 72 hours), which Simovic et al. (1985) attributed to volatilization of hydrogen cyanide. Total cyanide concentrations continued to decline, but at slower rates. These second parts of the total cyanide degradation curves varied among the metals and were assumed to be a result of different rates of dissociation or decay of the individual metallo-cyanide complexes. First-order reaction kinetics were assumed

15

and the second part of the curve was analyzed by linear regression to determine the metallo-cyanide decay coefficient (Table 2-18). Thus, Simovic et al. (1985) reported that the decay rate for the zinc-cyanide complex was the fastest under their test conditions (an order of magnitude more rapid than the copper-cyanide complex). The decay rate for the copper-cyanide complex was double that for the iron-cyanide complex, while the nickle-cyanide complex decay rate was an order of magnitude slower than the Cu-CN and Fe-CN complexes. Ultraviolet light affected the decay rate of only the iron-cyanide complex, so the other complexes might be expected to decay in the absence of light within spent ore bodies and in turbid waste tailings impoundments. Simovic and Snodgrass (1985) showed more of the data from these studies; residual total cyanide concentrations decreased to less than 1 mg/l within four days for the zinc-cyanide synthetic solution and within 12 days for the copper-cyanide solution; however, even after 15 days the total cyanide concentration was about 10 mg/l in the iron-cyanide solution, and the decay rate was so slow in the nickle-cyanide solution that the concentration had not decreased to less than 30 mg/l even after nine days. These data show that metal cyanide complexes do undergo dissociation reactions, but that the rates are very dependent upon the specific metal that is complexed. The zinc complex dissociates rapidly, but if nickel is present in the spent heap ore or vat tailings, the complexes formed will be more stable and the resultant total cyanide concentrations will be more persistent.

The release of cyanide from spent heap ores, vat tailings, and barren bleed solutions may occur by both aqueous and atmospheric routes. Surface water releases may result from run-on/run-off caused by storm events, unintentional/inadvertent overfilling of holding basins, or catastrophic events such as burst dams on the holding ponds for mill tailings or barren bleed solutions. Release to ground water can occur

Table 2-18. Degradation of Metallocyanide Complexes in Phosphate Buffer at pH 7[a]

| | $k_1 \times 10^2$ (4°C)[b] | $t_{1/2}$ (4°C)[c] | $k_1 \times 10^2$ (20°C)[b] | $t_{1/2}$ (20°C)[c] |
|---|---|---|---|---|
| $Zn(CN)_4^{-2}$ | 1.78 $hr^{-1}$ | 1.6 days | 4.49 $hr^{-1}$ | 0.64 days |
| $Cu(CN)_3^{-2}$ | 0.29 | 9.9 | 0.75 | 3.8 |
| $Fe(CN)_6^{-3}$ | 0.14 | 20.6 | 0.47 | 6.1 |
| $Ni(CN)_4^{-2}$ | 0.04 | 72.1 | 0.09 | 32.0 |

Source: [a] Initial concentration is 200 mg/l)
[b] Adapted and modified from Simovic et al. (1985).
[b] Half-lives were calculated from the rate constants.

from unlined impoundments at old or clandestine facilities. Release to ground water might also occur from percolation through breaks or fissures in liners below heap pads or lined lagoons. There are models available to predict the rate of seepage to ground water beneath tailings impoundments, but McWhorter and Nelson (1980) found the liner integrity and its retardation of release (i.e., hydraulic resistance to flow/passage through the liner) to be the single most important parameter influencing the seepage rates of releases from lined impoundments through the unsaturated zone into the saturated zone (ground-water aquifer). (See Chapter 3 for further details of ground-water release models.)

Most heap pads and pregnant solution ponds are designed and constructed to be well-lined, both because of the metal values contained in pregnant solutions and because of the costs of cyanide itself, however, problems and releases have occurred at some sites. In addition, it appears that precious metal recovery operations are designed on a site-specific basis, and that there is a lack of consistent design guidance relating to limiting releases to the ground water. In addition, the vast majority of facilities are in compliance with state or local regulatory requirements, but there are some clandestine, poorly designed operations in the vast uninhabited areas of the west.

Releases to the atmosphere are also possible; for example, see the discussion of the study of Stampfli (1986) conducted at the Annie Creek heap leach operation described in Section 2.2.4(1). Cyanidation is most efficient for leaching precious metals at alkaline pH values of 10.5 to 12, and the cyanide ion, the dominant species of free cyanide at those pHs, does not readily volatilize. However, in holding ponds, natural recarbonation can occur which results in the decrease of the pH to more neutral levels (pH 7). The dominant species of free cyanide shifts to the hydrogen cyanide form below about pH 9 and this form readily volatilizes. Catastrophic acidification of metallo-cyanide complexes might also occur under accidental conditions; this acidification could cause dissociation of the complex formation of hydrogen cyanide, and liberation of a cloud of hydrogen cyanide vapors. Losses from tailings ponds by volatilization have been documented (Schmidt 1981a, 1981b, Simovic et al. 1985), although catastrophic releases are only anecdotal (and probably very rare). Atmospheric sampling data, however, are not available, and long term, low level releases of cyanide from spent heap leach ore to the atmosphere have not been documented.

Only limited information is available on movement of free or complex cyanides at low concentrations out of spent ore piles or impoundments into the ground and/or their migration through the unsaturated and saturated zones. Free cyanides are able to migrate in soil, but their transport might be retarded because the cyanide would become complexed by trace metals and/or sorbed to clays or organic matter in the soil. In addition, low levels of free cyanide can be metabolized by various microorganisms (Fuller 1985). Under aerobic soil conditions, the prominent fate reaction for cyanide is nitrification. Under anaerobic conditions, the fate of cyanide includes attenuation by sorption, precipitation as metallo-cyanide complexes, microbial denitrification, and transport in sandy (low clay, low organic matter) soils.

In summary, the cyanide concentrations in the interstitial water are a function of a number of factors: metal speciation in the ore, metallo-cyanide complexes formed, water solubility of the complexes, dissociation rates of the complexes, amount of interstitial water and precipitation patterns, and rate of water flow/flushing, temperature, and rates of release of cyanide from the waste materials. The rates of release to the environment are a function of the following: form of the cyanide, pH of the waste material, permeability of the heap pad and/or impoundment liners, and temperature (which affects various natural degradation processes).

The following sections describe the limited data available on the fate and transformation of free cyanide and cyanide complexes in the waste materials and the documented releases from heap leaching and vat extraction facilities.

### 2.3.2 Assessment of Data on Cyanide Fate and Transport

An assessment of fate and transport for any chemical requires an evaluation of the relevant environmental processes that govern its structural transformations and its partitioning among environmental media. These processes include photolysis, hydrolysis, volatilization, sorption, bioaccumulation, and biotransformation/biodegradation. The analysis of these processes is usually systematized into a format that requires a discrete analysis of the chemical's potential for change within each individual process. In this way, the principal (or most rapid) processes that constitute the pathway(s) by which the chemical is environmentally dissipated can be identified. If the analysis is not organized in this (or a similar) format, there is no assurance that the chemical's environmental fate has been comprehensively assessed. The methodologies involved in this type of analysis and their application to specific chemicals are discussed in detail by Callahan et al. (1979).

Environmental information on cyanides, published from the precious metal industry, consists primarily of use patterns and monitoring (see Section 2.2). With few exceptions, notably Simovic et al. (1985), an evaluation of each of the fate processes acting in concert has not been presented. Therefore, for the purpose of constructing a comprehensive assessment, technical literature (not necessarily related to the precious metal industry) was surveyed through use of the Chemical Abstracts Service.

(1) Probable fate of cyanides in mining waste. A summary of environmental fate and transport processes is given in Table 2-19 for

Table 2-19 Summary of Environmental Fate and Transport of Cyanides from Mining Wastes

| Environmental process | Summary statement | Confidence of data |
|---|---|---|
| Photolysis | HCN is virtually unreactive in the troposphere and probably diffuses to the stratosphere before being destroyed. Some metallocyanides, e.g., ferrocyanide and ferricyanide, can be decomposed by sunlight in water to yield iron hydroxide and cyanide ion. | High |
| Oxidation | Free cyanide is not oxidized in air or water by molecular oxygen or hydroxyl radicals, but it is oxidized by polysulfides and polythionates in high sulfur ores to thiocyanate ion. Iron-rich ores may also promote the oxidation of cyanide through formation and decomposition of ferric ferricyanide, $Fe[Fe(CN)_6]$. | Medium |
| Hydrolysis | Hydrolysis of the CN bond of cyanide in mining wastes is too slow to be relevant as a fate process. Degradation of metallocyanide complexes can be considered to be their hydrolysis with release of cyanide ion. This latter process may be responsible for maintaining low levels of free cyanide in old waste piles. | High |
| Volatilization | If the alkalinity of liquid wastes is assumed to be pH 8-9, the half-life for volatilization of free cyanide is estimated to be 0.4 - 4.0 days. Volatilization from solid waste piles is much slower with a half-life that probably varies from several months to a few years. | Medium |
| Sorption | Free cyanide and most complex cyanides are sorbed to only a small extent and are therefore mobile in the environment. The exception is some complex cyanides which are sparingly soluble and are therefore apparently immobile. | High |
| Bioaccumulation | Free cyanide does not accumulate but some metallocyanides might accumulate in fish. | High |

Table 2-19. (Continued)

| Environmental process | Summary statement | Confidence of data |
|---|---|---|
| Biodegradation | Biodegradation of cyanides may be universal, but most organisms can only tolerate very low concentrations. Some microbial cultures can become acclimated to higher concentrations under aerobic conditions, but anaerobic degradation may proceed only at concentrations of a few parts per million. | High |

cyanides in the wastes generated during the processing of precious metal ores. Both the principal transport process and the most probable fate for free cyanide (i.e., HCN and $CN^-$) in these wastes are volatilization as hydrogen cyanide to the atmosphere. Although considered to be unreactive in the troposphere, hydrogen cyanide will diffuse upward and be destroyed in the stratosphere. Metallocyanide complexes will decompose at varying rates (albeit slower than the rates of volatilization) with the release of cyanide ion, which will then be present as free cyanide. Thus, this slower rate of decomposition of metallocyanides eventually becomes the rate controlling step for the volatilization of free cyanide as its concentration becomes lower than that of the metallocyanides. The secondary transport process for free cyanide and all soluble metallocyanide complexes is leaching. Leached cyanides may undergo biodegradation once they have diffused into the soil to a sufficient depth such that their concentration is no longer toxic to indigenous microorganisms. If leached cyanide levels do not become sufficiently low enough to permit biodegradation, cyanide could enter into the ground water. Free cyanide does not bioaccumulate but some metallocyanides might accumulate in fish. Cyanides are not generally persistent in the environment, although some sparingly soluble cyanide complexes of iron, cobalt, copper, and nickel may decompose very slowly in solid wastes and aquatic sediment.

(2) Identity of cyanide species in mining waste. Three types of cyanide-bearing wastes accumulate from the treatment of precious metal ores by the cyanidation process: (1) slurries and solutions discharged into tailings ponds or similar impoundments, (2) landfilled residual solids from conventional vat extraction, and (3) spent ore remaining from heap leaching operations (see Section 2.1). These wastes contain free cyanide (i.e., HCN and $CN^-$), minute amounts of precious metal cyanides, and some of the other metallocyanide complexes characteristic of the ore

undergoing extraction. The solid materials from vat extraction or heap leaching are often treated with water at the end of their contact time with the alkaline cyanidation fluid, so the level of free cyanide and soluble metal cyanides, as well as the pH, will be reduced in the spent ore and residual solids as compared to the level of these cyanides during cyanidation. Liquid wastes (i.e., fluids not recycled for further extraction) should contain most of the discarded free cyanide plus any soluble metallocyanides generated and not subsequently decomposed in the metal extraction process. In some large mining operations, these liquid wastes are subjected to a treatment process for attenuation of cyanide before being discharged to a tailings pond or other impoundment.

The relative amounts of hydrogen cyanide and cyanide ion, which constitute the free cyanide of the wastes, will depend on the pH of the waste material (Table 2-20). The $pK_a$ of HCN is 9.36 and the optimum pH for the cyanidation process is 10.3 (Huiatt 1985). During ore extraction, the alkaline pH is maintained in the process liquids by the addition of lime (CaO), calcium carbonate ($CaCO_3$), or sodium hydroxide (NaOH) to offset the neutralizing effect of carbon dioxide absorbed from the atmosphere. Solid wastes and discharged liquid wastes, however, will initially have a pH of about 10 as a result of water washing, treatment procedures, and dilution. In addition, these wastes will absorb carbon dioxide which will further reduce their pH values. The pH of exposed liquid wastes should eventually approach the pH of large bodies of mineral-buffered surface water. (The pH of the oceans is about 8.) Solid wastes will absorb carbon dioxide from the atmosphere much more slowly, at rates dependent on carbon dioxide diffusion into the heterogeneous, alkaline waste mass. A specific example (Engelhardt 1985, Milligan 1985a) of decreasing pH in an inactive leach heap is discussed in Section 2.3.3.1.

Table 2-20. Relationship of pH to Percent HCN in Free Cyanide ($CN^-$ plus HCN) of an Aqueous Solution

| pH | Percentage of free cyanide as HCN |
|---|---|
| <7 | >99 |
| 8 | 93.3 |
| 9 | 58 |
| 10 | 13 |

Source: Towill et al. 1978

Towill et al. (1978) reported the percentage of HCN in the free cyanide of an aqueous solution at various pH values (Table 2-20). At the pH of the cyanidation process (pH > 10), less than 13 percent of the free cyanide is present as HCN. Liquid wastes and the near-surface depths of solid wastes will rapidly become less alkaline because of carbon dioxide absorption from the atmosphere. At pH 9, the percentage of free cyanide as HCN is 58 and at pH 8, it is 93.3. The interior of solid waste piles and the sediments of impoundments, however, will probably maintain more alkaline pH values for a longer period of time.

The most common metal complexes in the wastes of gold and silver mining are those incorporating iron, copper, zinc, nickel, cobalt, and cadmium (Huiatt 1985). Other metal complexes, including those of gold and silver, will be present in comparatively minute amounts. Table 2-16 lists the relevant metal complexes in the order of their relative stabilities in water (Scott and Engels 1981). In general, the cyanide compounds of alkali and alkaline earth metals (Li, Na, K, Ca, Mg) are ionic and therefore dissociate in water; zinc and cadmium complexes decompose readily as free cyanide becomes depleted; and iron, nickel, cobalt, and copper complexes exhibit greater stability (Callahan et al. 1979, Simovic et al. 1985, Huiatt 1985). Cyanide complexes of the latter four metals can exist as supramolecular complexes in which the electrons of the cyanide group are shared covalently by more than one metal atom (Bailar 1956). These supramolecular complexes are resistant to dissociation.

According to Simovic et al. (1985), the degradation rate of the copper cyanide complex is double that of iron, while the degradation rate for the nickel complex is an order of magnitude slower than that of the copper or iron complexes. Iron, nickel, cobalt, and copper salts of the iron-complex cyanide ions (i.e., ferrocyanide and ferricyanide) are very sparingly soluble in water, but other environmentally relevant salts of these two complex ions are considered soluble (Weast 1977). Some copper and nickel cyanides are also sparingly soluble in water (Weast 1977).

As a consequence of these stabilities and solubilities in water, solid wastes from gold and silver mining could contain sparingly soluble cyanide complexes of iron, nickel, cobalt, and copper. Until their presence is exhausted, these cyanide complexes will degrade slowly to maintain a low concentration of free cyanide in the solid wastes. Although ferric ferricyanide is reported to decompose in the solid phase, it does not yield any form of cyanide ion (Huiatt 1985). In contrast, zinc and cadmium cyanides will probably decompose rapidly during the lifetime of the mining operation. Tailings ponds and other impoundments will contain most of the metal cyanide complexes listed in Table 2-16. As the free cyanide concentration in these bodies of water decreases, their cyanide complexes should decompose more rapidly.

(3) Persistence of cyanides in mining wastes and the surrounding environment.

(a) Impoundments and surface waters. Simovic et al. (1985) have reported that the two processes having the greatest effect on removal of total cyanide from gold mill impoundments are volatilization of HCN and release of cyanide ion from metallocyanide complexes. Since volatilization is a more rapid process than degradation of the complexes, and since the concentration of free cyanide in tailings or barrens ponds is much greater than the concentration of metallocyanides, the initial rate of removal is primarily the rate of HCN volatilization (Simovic et al. 1985). After several days, however, the concentration of free cyanide is sufficiently low to allow the degradation of metallocyanides to become the rate-limiting step in cyanide removal. The observed half-life for disappearance of free cyanide from surface waters was reported to be about 2 to 3 days. This value is in agreement with the half-life of 0.4 to 4 days for volatilization of HCN derived from the data of Broderius (1977) in Section 2.3.2(4d).

The half-lives for degradation of four metallocyanide complexes (Table 2-18), assumed to be the major chemical species in the mining effluents, were determined in a phosphate buffer at pH 7 (Simovic et al. 1985). The initial cyanide concentrations were 200 mg/l. The zinc complex degraded fastest (an order of magnitude more rapid than copper); the degradation rate of copper cyanide was double that of iron, while the rate for degradation of nickel cyanide was an order of magnitude slower than copper or iron. Both temperature and pH affected the rates of degradation of these complexes. The rates increased with increasing temperature (Table 2-18) but decreased with increasing pH. Simovic et al. (1985) attributed the differences of observed rates of metallocyanide degradation in mining effluents with those determined in bench-scale apparatus to be due to the effects of residual free cyanide, temperature, and pH. An additional factor, however, that would greatly decrease the degradation rates of metallocyanide complexes in mining effluents is their capability of existing in supramolecular forms that impede hydration and degradation (Bailar 1956). As an example, the iron, nickel, and copper salts of the iron-complex cyanide ions (i.e., ferricyanide and ferrocyanide) are very sparingly soluble in water (Weast 1977) and are probably present in the effluent as suspended solids or sediment. The degradation of these solids would not be as rapid as the degradation of the soluble complexes studied by Simovic et al. (1985).

After the liquids from mining impoundments are released to surface waters beyond the boundaries of the mining operation, volatilization should continue to be the most important process for removal of cyanide. The half-life for volatilization of free cyanide from surface water has been given as 8.8 to 55.5 hours (Broderius 1977). Some sparingly soluble metallocyanide complexes will degrade very slowly in surface water, but the amount of cyanide ion released by these complexes probably does not exceed the biodegradative capability of aquatic microorganisms.

Moore et al. (1979) reported the results of a field study on cyanide levels in surface waters that received cyanide waste. A set of three connected shallow lakes in the Canadian Northwest Territories received the decanted water from the liquid waste impoundment of a gold mine. After mining activities commenced in the spring of 1977, the lake into which the water was released reached a maximum of 0.5 mg/l of total cyanide in July. Thereafter, the cyanide level apparently decreased rapidly, since it was below the level of detection (i.e., 0.05 mg/l) in August and succeeding sampling months. Volatilization and biodegradation both were probably responsible for removal of cyanide from this lake. Cyanide levels in the two lakes downstream from the first remained below the level of detection during the entire sampling period.

(b) Leach heaps and landfills. Spent heap leach ores and residual tailings solids from vat extraction are washed to remove soluble precious metal cyanides at the end of their useful processing. Some of the complex cyanides, however, are sparingly soluble in water and would be expected to remain in the solid waste. These complexes (e.g., the iron, nickel, cobalt, or copper salts of ferricyanide and ferrocyanide) will decompose slowly with the release of cyanide ion. Both volatilization of HCN and release of cyanide ion from metallocyanides affect the rate of removal of total cyanide from mining effluents in impoundments (Simovic et al. 1985), although volatilization of HCN from leach heaps (and landfills) occurs so much more slowly than it does from impoundments that the effect of a relatively small amount of metallocyanide degradation should not be noticed. Furthermore, since the soluble metallocyanides would have been removed by washing, the leaching of solid mining wastes by rain water should mobilize only free cyanide. This free cyanide can be expected either to volatilize or to be biodegraded if its level of concentration decreases during diffusion into the soil. Groundwater could become contaminated, however, if soil concentrations of cyanide do not decrease to metabolizable levels.

Old piles of mining waste, such as those discussed in Section 2.2.4, may still contain some sparingly soluble metallocyanide complexes. The contribution that dissociation of these complexes made initially to the concentration level of free cyanide in the waste pile was probably very small, since these complexes are the most stable with regard to release of free cyanide. Subsequently, their degradation may be the only source of free cyanide in the old waste pile. However, the total amount of cyanide being released by these metallocyanides is smaller than it was originally.

Engelhardt (1985) reported on the decrease of cyanide levels in a set of inactive leach heaps. The pH in the heaps fell from approximately 10.5 at the cessation of operation in 1982 to approximately 9 in late 1984. Core samples were removed from the heaps and the entrained liquid was analyzed for cyanides. In January 1983, the heaps had 14.4 percent moisture, and the entrained liquid assayed 580 mg/l free cyanide. In September 1983, the moisture content was 13.6 percent, and the free cyanide level in the entrained liquid was 340 mg/l. Measurements in March 1984 disclosed a moisture content of 13.1 percent and a free cyanide level of 106 mg/l. This was an approximately 85 percent averaged loss of free cyanide from the heaps in 15 months. Engelhardt (1985) stated further that almost all of the total cyanide in the leach heaps could be accounted for as free cyanide.

(c) Atmosphere. Hydrogen cyanide is resistant to destruction in the troposphere (see Section 2.3.2(4a)). Because hydrogen cyanide is a gas that is lighter than air, however, Singh et al. (1984) consider it to be easily dissipated and assumed its eventual diffusion to the stratosphere.

(4) Fate and transport processes.

(a) Photolysis. Hydrogen cyanide is very resistant to photolysis by the wavelengths of light ($\lambda$ >290 nm) reaching the earth's troposphere (Frank and Bard 1977). In addition, the slow rate ($k < 10^{-15}$ $cm^3$ $molecule^{-1}$ $sec^{-1}$) at which molecules of HCN are reported to react with oxidizing species of the atmosphere (Phillips 1978), prompted Singh et al. (1984) to classify hydrogen cyanide as an airborne pollutant that is virtually unreactive in the troposphere. Hydrogen cyanide should eventually diffuse to the stratosphere, however, where higher-energy, shorter-wavelength, ionizing radiation will bring about its destruction.

The photodecomposition of ferricyanide and ferrocyanide solutions and resultant cyanide residuals in test solutions has been observed by Bandish and Bass (1922) and Schwarz and Tede (1927). This effect was corroborated by Burdick and Lipschuetz (1948) for river waters at concentration levels of 2 mg/l with both potassium ferrocyanide and ferricyanide. A 5-hour exposure of 100 mg/l potassium ferrocyanide to sunlight produced a cyanide ion level of 6 mg/l. Simovic et al. (1985) have reported that exposure to sunlight of aqueous metallocyanide complexes other than those containing iron (Table 2-18) did not result in release of cyanide ion.

(b) Oxidation. In gold and silver cyanidation wastes, direct oxidation of cyanides by molecular oxygen or hydroxyl radicals has not been reported as a significant process (van Zyl 1985). Sulfide minerals in the precious metal ores, however, do become oxidized to polysulfides and polythionates which then can oxidize free cyanide to thiocyanate (Huiatt 1985). Minimizing cyanide conversion to thiocyanate during the cyanidation process is one of the problems of precious metal mining. Another pathway by which cyanide can become oxidized in iron-rich ores is through the formation of ferric ferricyanide, $Fe[Fe(CN)_6]$. The CN radical of this compound is reported to decompose to $CO_2$ and $N_2$ without the release of cyanide ion (Huiatt 1985). If ferric iron (III) is reduced to ferrous iron (II) during this decomposition, it could be reoxidized by the dissolved oxygen in percolating water.

(c) Hydrolysis. The degradation of metallocyanide complexes by dissociation can be considered to be a hydrolysis reaction with displacement of cyanide ion by hydroxide ion on the metal center of the complex. This reaction is important to the environmental fate of cyanides in cyanidation wastes, since it affects the rate of cyanide removal from effluent impoundments. Table 2-18 gives the rate constants and half-lives of this reaction for four metallocyanide complexes investigated by Simovic et al. (1985) to be representative of the complexes present in mining effluents. These four metallocyanide complexes were soluble in water at the concentrations under which they were studied. Some of the cyanide complexes of these metals, however, exist in supramolecular forms that would impede degradation through hydrolysis (Bailar 1956). Therefore, the values in Table 2-18 should be considered maximum rate constants and minimum half-lives for metal complexes in actual mining wastes.

Hydrolysis of the CN bond also can result in the destruction of free cyanide, but it probably occurs slowly enough to be noncompetitive with other processes. Hydrolysis of HCN in strongly acidic solutions ($pH < 1$) proceeds with half-lives of 10 to 1000 hours (Kreible and McNally 1929). Cyanide ion can be hydrolyzed under alkaline conditions to formate ion and ammonia. Rate constants for decomposition range from $2 \times 10^{-8}$ $sec^{-1}$ to $2 \times 10^{-6}$ $sec^{-1}$ at temperatures between 33 °C and 65 °C (Wiegand and Tremelling 1972). The relatively slow rates reported for alkaline hydrolysis of free cyanide indicate that this process is not relevant for wastes from the cyanidation process.

(d) Volatilization. Hydrogen cyanide has been demonstrated to volatilize from samples of natural water with half-lives of 8.8 to 55.5 hours (Broderius 1977). The experiments were conducted with samples from 10 different sources of water. Spiked concentrations of cyanide ranged from 25 to 200 ug/l. Concentration levels of cyanide in the water were measured outdoors during a 6-hour period, from which half-lives were calculated for disappearance of HCN. When the HCN-spiked water samples were sealed and closed off from the atmosphere, disappearance of HCN became negligible. Singh et al. (1984) have classified hydrogen cyanide as a pollutant that will rapidly volatilize and become dissipated in the atmosphere.

Since mining wastes from the cyanidation process have alkaline pH values, only part of the free cyanide is present as HCN (Table 2-20). Inasmuch as absorption of atmospheric carbon dioxide rapidly decreases the pH of these wastes to pH 8-9, the half-lives for volatilization given by Broderius (1977) must be increased to 0.4 to 4.0 days (based on concentration of free cyanide). This half-life for volatilization of HCN from water may be applicable to liquid wastes. Volatilization from the solid wastes, however, is limited by diffusion of HCN from the mass of the waste pile to its surface. Cruz et al. (1974) and Alesii and Fuller (1976) have shown that the adsorption of HCN to dry or wet clay and soils is very weak. Therefore, outward diffusion of HCN from the waste pile should not be impeded by sorptive interactions. Loss of HCN from an inactive leach heap is discussed in Section 2.3.3.1.

(e) Sorption. Free and complexed cyanides are sorbed to a small extent by a variety of materials, including clays (Cruz et al. 1974, Schenk and Wilke 1984), soils (Alesii and Fuller 1976, Fuller 1985) sludge (Raef, et al. 1977a), and plant debris (Schenk and Wilke 1984). Free cyanide, however, is not greatly partitioned from water to any of these solid materials, and it is therefore considered that free cyanide is very mobile in the environment. Fuller (1985) has determined that potassium cyanide (KCN) and certain ionic complexes, e.g., $K_3Fe(CN)_6$, are mobile except in soils having a high concentration of hydrous oxides of iron. In contrast, the free cyanide added to the landfill leachate was much less mobile than either of the ionic cyanides (in distilled water). Presumably, this decreased mobility was due to formation in the leachate of insoluble cyanide complexes. Mobility of cyanides is greatest in soil at high pH (high negative charge) and low clay content.

Raef et al. (1977a) found that flocculating bacterial cultures could remove only small amounts of cyanide from solution by sorption; nonflocculating cultures apparently could not remove any detectable quantity of cyanide. It was concluded from these observations that sorptive phenomena were not important for the removal of cyanide in a sewage treatment facility.

(f) Bioaccumulation. Broderius (1973) has reported the accumulation of metallocyanide complexes in fish. Copper cyanide concentrations ranged from undetectable to 303.9 ug per gram for various bluegill tissues, with the liver and gall bladder fraction exhibiting the greatest bioaccumulation. Likewise, silver cyanide was accumulated in concentrations up to 168.4 ug per gram. Accumulation of free cyanide, however, does not occur in animals because it is metabolized at low levels and becomes toxic at higher levels.

Accumulation of cyanide does occur in some plants (e.g., sorghum), but not as a result of increased absorption from the environment. Cyanide exists naturally in many plants as part of their complex carbohydrates (Reed 1985). Hydrogen cyanide is released when these carbohydrates are enzymatically hydrolyzed by the plant or when they are catabolized by animals that have eaten the plants. Accumulation of these cyanogenic carbohydrates is enhanced in some plants under conditions of environmental stress such as drought, frost, or growth-stunting disease (Fuller 1985).

(g) Biodegradation. Hydrogen cyanide, metallocyanide complexes, and cyanogenic carbohydrates are all subject to biodegradation. It has been demonstrated that activated sludge treatment can result in virtually complete removal of cyanide (Ludzack and Schaffer 1962, Kostenbalder and Flecksteiner 1969), but Raef et al. (1977b) contended that most of the loss of cyanide in such systems is due to stripping (volatilization).

The ability to biodegrade hydrogen cyanide or its salts at non-toxic concentrations appears to be nearly universal (Reed 1985). A bacterium has been isolated that is capable of using cyanide as its sole source of carbon and nitrogen (Ware and Painter 1955), but most organisms can only tolerate very low concentrations. Typical metabolic pathways for degradation of cyanide include production of thiocyanate, reaction with hydroxocobalamin to form cyanocobalamin, combination with amino acids, and oxidation to carbon dioxide and formate ion (Towill et al. 1978). Hydrogen cyanide is also synthesized by a variety of soil organisms, including bacteria (Lorck 1948, Wissing 1974, Castric 1975), fungi (Hutchinson 1973), and a millipede (Duffey and Bium 1977).

Nowak and Chmielowski (1975) reported the successful adaptation of a mixed microbial culture to use free cyanide ion as its sole source of carbon, nitrogen, and energy. Approximately 50 percent of the carbon was oxidized to carbon dioxide and 50 percent was incorporated into cellular biomass. The nitrogen was transformed into ammonia, nitrite, and nitrate. Oi and Yamamoto (1977) isolated a Streptomyces species that was capable of oxidizing cyanide ion to thiocyanate in the presence of sodium thiosulfate. Harris and Knowles (1983a, 1983b) reported the isolation of a strain of Pseudomonas fluorescens that utilizes cyanide as a source of nitrogen under aerobic conditions. Isolation of the bacteria from soil, sediment, or sludge required the maintenance of a sub-inhibitory concentration of cyanide in the growth medium for several days.

Cyanide-reducing enzymes have been extracted from the bacteria Azotobacter vinelandii and Clostridium pasteurnianum (Hardy and Knight 1967). Under reducing conditions, these enzymes were shown to be capable of catalyzing the reduction of HCN to $CH_4$, $NH_3$, and possibly small amounts of $CH_3NH_2$. Adenosine triphosphate (ATP) was required for the reaction, and it was necessary for the enzymes to be extracted from cells grown with $N_2$, rather than ammonia or urea.

Soil microorganisms capable of degrading cyanide under anaerobic conditions are thought to be inhibited by cyanide concentrations that would be tolerated by organisms growing in aerobic environments (Fuller 1985). Although studies on the anaerobic microbial degradation of cyanide in soil have not been conducted, the upper limit for anaerobic degradation of cyanide concentrations in a sewage wastestream has been determined to be 2 ppm (Coburn 1949). If this greater toxicity of cyanide to anaerobic microorganisms is also valid in soil, it should be necessary for free cyanide in anaerobic soil to diffuse and be diulted to a sufficiently low, nontoxic concentration before biodegradation can occur.

### 2.3.3 Assessment of Reported Data on Releases

The following subsections present an evaluation of environmentally relevant data concerning releases of cyanides from mining wastes. Some of the information was submitted by the precious metal mining industry. These and other submissions are listed in Table 2-21. Some of the submissions listed in Table 2-21 did not contain monitoring or fate and transport data and were, therefore, not evaluated for incorporation into this report.

Table 2-21 Materials Received from Various Submitters Concerning Cyanide-Bearing Mining Wastes

| Submitter | Date | | Materials received^a |
|---|---|---|---|
| Dr. James L. Hendrix<br>University of Nevada - Reno | 1/28/86 | (1) | Quarterly report to BOM re tailings ponds cyanide concentrations |
| Fred DeVries<br>duPont | 1/27/86 | | Cyanide handling (background information) - materials |
| Jean Moore<br>Bureau of Mines | 2/7/86 | | Cyanide wastes production data for 1974-78 |
| Bill Fellows<br>Education & Training Coordinator<br>Office of State Mine Inspections<br>Arizona | 2/12/86 | | Worker safety slide show, and list of four neighboring State's coordinators |
| Luther Russell<br>Environmental Coordinator<br>Superior Mining | 2/19/86 | | Letter to Senator Symms re Report to Congress |
| Rick Richins<br>James M. Montgomery, Consulting Engineers, Inc. | 2/20/86 | | Availability of data |
| F. DeVries, transmitting for<br>T. J. Smolik of<br>Golden Sunlight Mines (2/14/86) | 2/25/86 | | Handling information and inter-laboratory test results |
| J. D. McBeth<br>Carlin Gold Mining Company | 2/24/86 | | Handling data and suggestion of sampling results |
| Marion F. Ely, II<br>Consultant to California company | 3/18/86 | (2) | "Cleanup and Abatement" at American Mine (heap leach) |
| Luther Russell<br>Environmental Coordinator<br>Superior Mining (Second submittal) | 3/17/86 | | Letter to Senator McClure re Report to Congress (some new ideas) |

0770E

Table 2-21 (Continued)

| Submitter | Date | Materials received* |
|---|---|---|
| F. DeVries<br>duPont | dated 3/17/86<br>rec'd 3/25/86 | Letter re issues and three reports:<br>(3) Australian vat mill data<br>(4) Data from old Homestake tailings<br>(5) duPont computer model runs on EPA lagoon model |
| Kent McGrew<br>Wharf Resources at Annie Creek Mine, SD | phone 3/17/86<br>mailed 3/26/86 | (6) 1. Ambient air data report<br>(7) 2. Lysimeter data reports<br>(8) 3. Small column neutralization tests report<br>4. Letter to State re site neutralization data, and<br>5. 2nd letter to State re site neutralization data |
| Allan Young<br>Sunshine Mining Company to Dexter Hinkley | dated 3/17/86<br>rec'd 3/31/86 | (9) 1. Cyanide mill permit<br>2. Permit data<br>3. Data on water in wells and sampling |
| Rick Richins<br>James M. Montgomery, Consulting Engineers, Inc. | dated 3/26/86<br>mailed 3/28/86 | (10) 11 pp. letter to Docket Clerk re Report to Congress |
| John Pahlman<br>U.S. Bureau of Mines | dated 3/28/86 | (11) Tombstone Silver Mines, Inc. - spent heap leach cyanide data |
| Jon Sprague<br>Barrick Mercur Gold Mines | 4/2/86 | (12) Memo 3/19/86 and Report 4/1/86 concerning sampling of 1890's mill tailings |

6

Table 2-21 (Continued)

| Submitter | Date | Materials received* |
|---|---|---|
| James McCutchan<br>State Mine Inspector<br>State of Arizona | 1/27/86<br>mailed 2/4/86 | 1. Annual Report of Office of Mine Inspector<br>2. Safety Education Plan<br>3. Booklet on Arizona State Cyanide Health and Safety Procedures<br>4. Arizona Regulations (2 sets)<br>5. Newspaper article and 2 trade journal articles<br>6. Paper by Donald Baker on Cyanide Use in the Mining Industry<br>7. "Post Operating Treatment of Cyanide ($CM^-$) solutions in Leaching Operations", 4 pp. - Office of State Mine Inspector |
| R.T. Richins<br>Governmental Affairs Manager<br>Coeur d'Alene Mines Corp.<br>and<br>Luther Russell<br>Environmental Coordinator<br>Superior Mining Company | 5/12/86 | Letter that lists the components of three ongoing projects:<br>1. Analysis of ore at various stages<br>2. Monitoring of treated ore<br>3. Land application of treated wastes |

* (Numbers in parentheses correspond to environmental data concerning cyanide bearing wastes.)

### 2.3.3.1 Heap Leaching Sites and Releases of Cyanide

Over the last decade there has been a considerable increase in the amount of ore being processed for precious metal extraction by heap leaching (Table 2-4), as well as an increase in the number of locations where these heap leaching operations are being conducted. Section 2.2.1 describes these recent trends and indicates possible increases in the near future.

The 1984 Minerals Yearbook (Lucas 1985a) reported environmental problems at three of the many sites where gold is extracted by heap leaching. There was a court-ordered closure because of unspecified objections on environmental grounds of the Yuma Mine, west of Tucson, where Consolidated Mining and Milling Ltd. had constructed heap leaching facilities to recover gold from the dump containing tailings from the old mine. Unspecified environmental problems reportedly led Tombstone Exploration Inc. to close its open pit gold and silver mine at Tombstone, where pelletizing of the heap materials had been employed to aid the heap leaching operations (Engineering and Mining Journal 1981b). The new Annie Creek open-pit, heap leach operation was temporarily shut down voluntarily because of concerns by the operator (Wharf Resources (USA) Inc.) that heavy summer rains might exceed the holding capacity of leachate ponds.

Other potential problems involving environmental releases from heap leaching and other cyanidation operations have been identified by SCS Engineering, Inc. (1985) (reviewed by TRC Environmental Consultants, Inc. (1985)). The types of problems encountered have included seepage from tailings ponds contaminating soil and/or ground water; rain fall or snowmelt causing overflow of ponds, resulting in discharges to surface waters and degradation of water quality and/or fish kills; improperly disposed of drums and unfenced ponds allowing wildlife (deer and birds) to consume cyanide solutions, ingestion which resulted in death of wildlife. The damage case incidents described cannot be viewed as an indication of widespread problems associated with cyanide leaching operations, although their geographic distribution suggests a pattern of more than minor, isolated problems.

Most of the release incidents identified are associated with leachate holding ponds. Another hypothetical source of release is the percolation of water through spent heap leach ores causing the migration of free cyanide or metallo-cyanide complexes and their escape to the environment. If there were any residual cyanides in spent ore left on the leaching pad, the cyanide is not likely to escape directly into the ground below the pad because the mining engineers should have constructed the pad to be impervious to aqueous solutions. However, there are apparently very little data available on the sampling and analysis of cyanides in the unsaturated or saturated zones below heap leach pads, so the assumption of minimal releases cannot be substantiated with adequate supporting data. The caustic conditions of highly alkaline pH may, in fact, contribute to the chemical breakdown and failure of the liner. Bond and Rouse (1985) described the applicability of pressure/vacuum lysimeters at heap leaching and tailings sites, but only one precious metal cyanidation site was described where lysimeters were used and no analysis data were presented. Leachate generated by rain percolating through the spent ore may mobilize sorbed or formerly insoluble metallo-cyanide complexes, or free cyanide may be liberated. Rain falling on spent ore remaining on the pad after the termination of leaching could generate leachate, which could run-off into the former pregnant solution basin. This basin would also have been constructed with an impervious liner so that direct escape to the ground would be unlikely but, as with the heap leach pads, there are no lysimeter data available to support the assumption of completely impermeable liners in the holding ponds. Run-on and runoff problems caused by unusual storm events may result in overflow of holding basins.

Spent ore removed from the impervious heap pad and dumped on bare ground may be a potential source of release of cyanide-bearing leachate. This leachate is much more likely to percolate into the ground than the cyanide in a lined impoundment or on an impervious heap pad. This discussion of release and transport of cyanide from spent heap leach ore pile dumps is hypothetical, however, because there is very little information, either on cyanide mobility in spent ore, or on release of cyanide from the spent ore. Similarly, there is very little information on the atmospheric releases of cyanide from spent ore or from abandoned holding ponds. Photodegradation of metallo-cyanide complexes is obviously not likely within spent ore bodies, but at the surface of heaps and within holding ponds there may be ultraviolet-light-catalyzed liberation of cyanide ions and, depending on the pH, formation of hydrogen cyanide, the species that is more volatile than the cyanide ion.

There are no mathematical models available describing the fate and transport of cyanide and/or metallo-cyanide complexes released from spent ores from heap leach processes. Time-series data of cyanide concentrations within spent ore are available from only one former heap-leach operation (Engelhardt 1985, Milligan 1985a). Sampling began three months after termination of heap leaching operations. At that time, about 11.5 percent of the cyanide which had been applied to the heap still remained in the spent ore after processing and washing with water, so the time-series study was conducted to follow natural dissipation of cyanide levels. Samples were collected with a 3.8-centimeter (1.5-inch) pipe driven through the heap into the pad. Samples were agitated for one hour with distilled water and the slurry was filtered to recover the solution. Following pH adjustment to 12.0, the samples were analyzed for free cyanide. Data collected at 3 and 18 months after termination (i.e., 15 months between samplings) indicated that most sampling cores showed substantial decreases in the free cyanide concentrations, with the percentage decreases ranging from 16.9 to 93.4 percent (Table 2-6). It was reported that there was a small difference between total and free cyanide concentrations (total was "almost the same number as the free assay"), but total cyanide concentrations data were not reported. It was reported that 1.0 mg of free cyanide per kg of solids would represent degraded heap leach cyanide levels and that "at the present rate of degradation, it will take approximately four years to attain this level" (i.e., 1 mg/kg). The only sampling data reported, however, are shown in Table 2-6, and these data do not provide a strong basis for this estimation of degradation rates or the final concentration values four years after termination of leaching.

M. F. Ely, II (1986) reported on cleanup and abatement following leakage from an inactive heap (American Mine Operators) in the Mojave Desert, California. Breaks in the PVC liners used below several inactive leach heaps allowed rainwater to percolate from the heaps and into the soil at 59 measured locations. Soil core samples were analyzed for free cyanide, and it was found that maximum penetration into the soil ranged from 18 to 24 inches. Free cyanide was measured by the silver nitrate titration method. Two of the four heaps had been idle for more than two years, and these heap materials themselves contained no measurable free cyanide. Heap materials collected at the two other heaps showed many depth-column samples with no free cyanides, but free cyanide concentrations in other samples ranged from 10 to 150 ppm. The depth/spatial pattern of the elevated concentrations appeared to be random.

Ely (1986) also reported that both water and sediment samples were collected in the barren and pregnant solution ponds below the inactive heaps, as well as from the soils adjacent to and below the ponds, because there had been breaks in these PVC liners as well. Free cyanide was not detected in water from the barren pond, but the very alkaline sediment from the pond contained up to 500 ppm free cyanide. Liner failures below the barren, pregnant, and overflow ponds occurred, and free cyanide was detected in soil cores collected from each of these locations. Free cyanide concentrations of up to 300 ppm were measured in the soil cores below the ponds and, as below the heap pads, the maximum depth of free cyanide detection was 24 inches. The water table at this site is very deep, because earlier attempts to find water resulted in a 440-foot dry hole.

Ely (1986) also reported free cyanide concentrations in the leachates from the inactive heaps at the American Mine. The leachates were aerated while traveling 1,000 to 2,000 feet through open ditches, and the concentrations decreased during passage down the ditch from 50 ppm to below the level of detection. Volatilization was considered to be the most important natural process for removal of cyanide from these heaps, ponds, and drainage ditches, and losses of the cyanide that percolated into the soil were accounted for by natural degradation processes (presumably the processes of biological and chemical breakdown).

In summary, while heap leaching is now the predominant method of cyanidation, very little information is available on the following: the disposition of the liquids in the barren bleed pond at closure; the long-term fate of free and total cyanides remaining in the spent ore; and the potential releases and environmental transport of cyanides originating from spent heap leach ore and the barren bleed solution ponds.

#### 2.3.3.2 Vat Extraction Sites and Releases of Cyanide

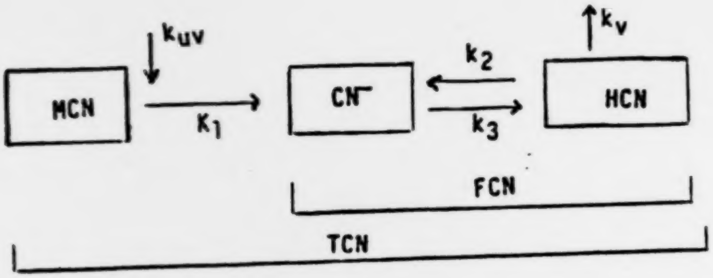
Scientists from Environment Canada's Wastewater Technology Center at Burlington, Ontario developed a mathematical model with predictive capabilities to describe the natural degradation of cyanide in the various wastewater effluent streams originating from vat extraction gold mills (Simovic et al. 1985, Simovic and Snodgrass 1985). The model (Figure 2-1) developed was based on the following information:

1. Metallo-cyanide complexes (MCN) dissociate into metallic and cyanide ions ($MCN \rightarrow M^+ + CN^-$).
2. Cyanide ions combine in a hydrolytic reaction with the hydrogen in water, and form HCN. The equilibrium developed between $CN^-$ and HCN is pH-dependent.
3. Molecular HCN is the species that volatilizes. Gold extraction operations are conducted under alkaline conditions, but the waste waters may undergo natural recarbonation and, with a decrease in pH, the dominant form of free cyanide is HCN. As pH approaches 7.0, the volatility of HCN becomes the predominate loss mechanism.
4. The rates of dissociation of metallo-cyanide complexes are affected by temperature, with decay proceeding more rapidly at higher temperatures.
5. Ultraviolet radiation may affect the dissociation of some metallo-cyanide complexes, especially those with iron.
6. Chemical oxidation of HCN to form cyanate does not appear to be an important degradation mechanism. Biological oxidation of cyanide does not appear to be important in tailings pond systems (Simovic and Snodgrass 1985).

Synthetic solutions of simple cyanide (NaCN) and metallo-cyanide complexes of Cu, Zn, Ni, and Fe were used in laboratory tests to examine factors influencing the natural removal of cyanides and to generate data for estimating kinetic parameters for the model (Simovic et al. 1985, Simovic and Snodgrass 1985). The test solutions were buffered at pH 7, which is lower than the pH in most tailings impoundments.

The most important mechanism in natural degradation of cyanide (i.e., loss of free cyanide from solution) was found to be volatilization. Among the variables affecting the degradation process, three were identified as the most important and selected for study,

95



where: MCN = metallo-cyanide complex

TCN = total cyanide

FCN = free cyanide

$K_1$, $k_2$, $k_3$ = rate constants ($h^{-1}$) of transformation

$k_{uv}$ = effect on k, due to ultraviolet irradiation ($h^{-1}$)

$k_v$ = volatilization mass transfer coefficient (cm/h)

Figure 2-1. Cyanide Degradation Model
(Simovic et al. 1985; Simovic and Snodgrass 1985)

including temperature, ultraviolet light, and aeration. Temperature had the largest effect upon reaction kinetics and, for the iron-cyanide metallo-complex, ultraviolet irradiation also had a significant effect upon the decay rate. Chemical oxidation had been found to be a loss mechanism in preliminary field studies (volatilization accounted for 90 percent of the loss, and chemical oxidation for 10 percent), but the laboratory studies with synthetic solutions provided data that indicated chemical oxidation of cyanide to cyanate was not an important loss mechanism.

The model assumed that the decay rate of a metallo-cyanide complex and subsequent volatilization rate of HCN (hydrocyanic acid) control the disappearance of total cyanide from solution, with metallo-cyanide decay being the rate-controlling factor. Sudden decreases in cyanide concentrations in all tests solutions within the first 24 hours were attributed to release of HCN from solution by volatilization.

The model fit the experimental data for the synthetic, single metallo-cyanide solutions with 95 percent confidence level for five of the eight tests (Simovic et al. 1985) and a range of $R^2$ values from 0.93 to 0.99 for most of the experiments (Simovic and Snodgrass 1985). These results provide some validation of the model, but both of the studies reported that some experiments exhibited inconsistencies in the estimated volatilization coefficients, which varied too widely.

Simovic et al. (1985) utilized the model developed from these synthetic solutions to test data derived in batch systems of waste water effluents from two Canadian gold mines; one was a barren solution (a bench scale experiment in an aerated 2-liter graduated cylinder) and the other was tailings pond water (a field experiment in an aerated, open circular tank 1.6-meters deep and 7.3 meters in diameter). The barren solution bench test showed decreases in the total cyanide concentration from 145 mg/l to about 30 mg/l in about 4 days, to about 7 mg/l in about 20 days, and after 1,320 hours (55 days), the total cyanide concentration was 2.3 mg/l. Simovic et al. (1985) applied their model to these data, and adjusted the volatilization rate to account for the pH dependent speciation of HCN (the model's calibration had been based on synthetic solutions at pH 7, but the barren solution bench test was initiated at pH 11.5 and recarbonation resulting from aeration caused the pH to decrease to 8.2). The model was similarly recalibrated to account for the different metallo-cyanide complexes present in the barren solution bench test, complexes which degraded more slowly than the complexes tested in the synthetic solutions used for initial model calibration. At the higher pH values tested, any free cyanide formed by dissociation of metallo-cyanide complexes would form the cyanide ion and could complex another metal; not much of the free cyanide liberated would form substantial amounts of HCN and, thus, not much of the free cyanide would volatilize.

Simovic et al. (1985) reported the model prediction for the tailings pond water was considerably better than for the barren solution. Total cyanide concentrations tested were much lower than in the barren solution bench test and the initial pH values were much lower; Simovic (1984) stated that the effluent in this tank was not a "typical" sample from the tailings ponds of that mill because of either dilution or metallo-cyanide degradation processes. The initial 4.3 mg/l total cyanide concentration had decreased to measured concentrations of less than 2 mg/l in about 7 days, about 0.5 mg/l in about 2 weeks; the reported total cyanide concentration was 0.2 mg/l after 65 days. The model predicted a slow degradation rate for total cyanide and, thus, the model-estimated total cyanide concentrations were somewhat higher than the measured concentrations just described, at least for earlier test intervals. Conversely, after about 40 days, the observed total cyanide concentrations of 0.2-0.3 mg/l were greater than the predicted concentrations of 0.05-0.10 mg/l.

Simovic et al. (1985) further extrapolated their modeling efforts to predict the degradation times for representative wastewater systems at two Canadian gold mills. One wastewater system was a batch system, a holding pond filled with barren solution and allowed to naturally degrade the cyanide until the total cyanide concentration is 0.05 mg/l prior to its discharge into receiving waters. The retention time required to achieve this effluent objective was calculated to be 5.8 months at summer conditions of 20 °C and 12.5 months at winter conditions of 4 °C. No holding pond in Canada would remain at that temperature for one year; moreover, most Canadian gold mills fill these holding ponds during the winter. The wastewater pond freezes solid rapidly and the barren solution is then held until the end of the following summer, at which time the pond waters are discharged. These model results were compared with data of Schmidt et al. (1981b) that reported actual results for a Canadian gold mill barren solution holding pond (volume = 6,000 $m^3$) where a concentration of 0.05 mg/l was reached after 5.5 months. These results agree well with the model-calculated prediction of 5.8 months (Simovic et al. 1985).

The other field system modeled by Simovic et al. (1985) was a tailings pond, represented by a continuous stirred tank reactor with a continuous inflow, a 3-day retention time, and discharge to receiving waters. Influent total cyanide concentrations were assumed to be 22.3 mg/l and 14 mg/l in summer and winter, respectively. After 3 days' retention, the total cyanide concentrations remaining (and percentage removals) were predicted to be 12.7 mg/l (43 percent removal) and 9.4 mg/l (32.9 percent removal) for summer and winter, respectively. These predicted wastewater effluent concentrations would appear to remain unacceptably high compared with water quality criteria for cyanide. Even

99

after 30 days' retention time, the total cyanide concentrations were predicted to be 3.9 mg/l (82.5 percent removal) and 3.9 mg/l (72.1 percent removal) for summer and winter, respectively.

The modeling results presented by Simovic and coworkers from Environment Canada (Simovic et al. 1985, Simovic and Snodgrass 1985) are very useful for predicting the natural degradation of cyanide in tailings holding ponds and barren solution ponds, especially where the modeling predictions are compared with actual field data that Simovic and her coworkers have reported for time-series cyanide concentration data for such ponds.

A report by DuPont (1985) described mathematical modeling of cyanide removal from a tailings pond to predict the rates of removal of free cyanide from shallow (<2 feet) and deep (15 feet) ponds. Volatilization was assumed to be the principal path for removal of cyanide, since hydrolysis under conditions of a tailings pond would be very much slower. Although the models can be calculated using various pH and temperature values, the rate of pH decrease due to absorption of atmospheric carbon dioxide was not considered. Additionally, metallocyanide complexes are assumed to remain at the bottom of the ponds and are not included in the models. Therefore, the models will probably have a limited use for describing or predicting the actual environmental fate of cyanide in mining wastes. The modeling approach of Simovic et al. (1985) should be more useful, because it includes both aqueous absorption of carbon dioxide from the atmosphere and degradation of the metallocyanide complexes.

Hendrix and coworkers at the University of Nevada-Reno have also conducted time-series sampling and analysis studies on tailings ponds in Nevada (Table 2-9; Section 2.2.4). Early efforts (Hendrix et al. 1985) were directed at developing of the field collection of samples and the laboratory extraction and analysis of the samples. The early data in Section 2.2.4 describe one tailings pond, but more recent data for time-series sampling and analysis of other tailings pond systems are not yet available.

The primary loss mechanism from vat leaching solid and liquid waste appears to be volatilization of HCN; the fate of the cyanide in the atmosphere deserves further attention. In addition, the modeling studies of Canadian vat leaching operations may well be representative of the types of wastes generated by well-operated systems in the United States, but further time-series data on natural degradation within wastewater systems in U.S. mills would certainly be useful.

One aspect not addressed by the Canadian modeling efforts is the unintentional releases from vat leaching wastewater systems. For example, barren solution storage ponds and tailings ponds are usually constructed with appropriate liners comprised of materials not readily attacked by free cyanide, metallo-cyanide complexes, or other substances likely to be present in these wastewaters. Under certain unintentional circumstances, a failure of the liner and percolation into the ground may occur, with potential transport via the unsaturated zone to ground water or nearby surface waters. During periods of heavy rainfall, run-on into the ponds may occur, filling the ponds above their freeboard and causing overflow. Catastrophic wastewater releases might also occur because of the bursting of dams within tailings impoundments or barren bleed solution ponds.

The 1984 Minerals Yearbook (Lucas 1985a) reported that there had been a cyanide leak from the holding pond at the Grey Eagle Mine in Siskiyou County, California. In September, 1983, a cease-and-desist court order was filed against the operator, Noranda Grey Eagle Mines, Inc. This order was dropped by the Regional Water Quality Control Board in October

1984 in exchange for an agreement by the company to conduct a 30-year cleanup and reclamation program following closure of the mine site in about two years from the date of the agreement.

Young (1986) reported on monitoring of a tailings disposal facility near Silver Peak, Nevada, by Sunshine Mining Co. The monitoring program consisted of two parts: (1) analysis of water samples collected from a 400-meter well located 1,700 feet from the tailings impoundment, and (2) examination of shallow 3-meter wells adjacent to and below the tailings impoundment. The shallow wells were dry for every monthly sampling date, suggesting no seepage from the tailings impoundment. For 4 1/2 years (June 19, 1981 to January 1, 1986), the potable water samples from the 400-meter well were analyzed as having cyanide concentrations of less than detectable except for a monthly few samples. Most of the samples had a concentration of <0.005 mg/l, but there were four samples of 0.005 mg/l, and four others ranging from 0.009 to 0.026 mg/l. The three anomalous values (greater than 0.01 mg/l) were attributed by Young (1986) to sample bottle contamination. The monitoring data and laboratory sheets did not indicate whether the analyses were total or free cyanide, but the analysis method was presumably for total cyanide, because this is the form specified in Sunshine Mining Co.'s State of Nevada "Zero Discharge Permit."

### 2.3.4 Treatment of Cyanide-Bearing Wastes

Various methods are available for the treatment and degradation of cyanide in spent ores and vat tailings (Schmidt et al. 1981a, 1981b, Schiller 1983, Scott 1985, Intermountain Soils, Inc. 1985, Milligan 1985a). These include:

- Alkaline chlorination (percolation with a NaOCl or $Ca(OCl)_2$ solution or injection of chlorine gas).

102

- $SO_2$-air mixtures at controlled pH (about 9-10) in the presence of copper as a catalyst as developed by Inco Metals Company.
- A biological process on liquid wastes that involves rotating biological contactors at the wastewater treatment facility (employed by Homestake Mining Company at Lead, South Dakota on their combined mine water and tailings impoundment wastewater).
- Destruction of the cyanide by oxidation with hydrogen peroxide ($H_2O_2$).
- An iron sulfide process to bind the free and complexed cyanides.
- Acidification to remove the cyanides by volatilization of HCN (although this procedure may have applications for only specialized ores because of the potential for rapid formation of a cloud of the toxic hydrogen cyanide gas).
- Natural degradation by evaporation of the free cyanides as is practiced at zero discharge wastewater facilities.
- Other natural degradation removals including photodecomposition, chemical oxidation, hydrolysis, precipitation by naturally occurring substances, adsorption of cyanides onto solids, and microbial degradation. Only a few precious metal extraction facilities utilize any treatment/destruction process for cyanide-bearing wastes other than natural degradation.

### 2.3.5 Conclusions

Only limited information is available on time-series degradation of cyanide-bearing wastes at heap leaching and vat leaching facilities. Apparently only one heap has been analyzed at various times for cyanide concentrations. Data are available on the cyanide wastes at two Canadian vat leaching gold mills, but it is not clear whether the data from these facilities are representative of U.S. vat leaching wastes.

Data on environmental releases of cyanide are very limited, but this paucity of data does not necessarily mean that such releases do not occur in more locations than have been identified in this report. The technology is available to treat cyanide-bearing wastes, but current indications (Scott 1984) are that these processes are being used at only a few of the facilities where cyanidation is employed for extraction of precious metals.

The conclusions on fate and transport were based on the available scientific literature and based on data submitted by the mining industry. The data were not suitable for an evaluation of individual fate processes, although the industry data serve to corroborate the conclusions that could be drawn concerning the composite of the fate processes. Data submitted by industry consisted primarily of field monitoring, which does not address individual fate processes.

The principal fate and transport process of cyanide used in extraction of precious metals from ores is volatilization as hydrogen cyanide to the atmosphere. This substance is considered to be photolytically stable in the troposphere, but it is assumed to be destroyed after its diffusion to the stratosphere. Residual metallocyanides in the mining wastes decompose at widely varying rates to release additional amounts of free cyanide. This continuing generation of cyanide ion, after most of the free cyanide initially present in the wastes has volatilized, can maintain a low concentration level of free cyanide until all the metallocyanides are exhausted. Both alkaline and acidic conditions apparently enhance the release of cyanide ion from metallocyanide complexes, but alkaline conditions will impede transport of free cyanide by volatilization. The metallocyanides that are considered to be the most stable with respect to degradation in mining wastes are the sparingly soluble complexes of iron, nickel, cobalt, and copper.

The secondary transport process for cyanide in mining wastes is leaching. Free cyanide and readily soluble metallocyanides can be transported through the soil with runoff water. Cyanides in the soil should undergo biodegradation once they have diffused sufficiently for their concentration to be no longer toxic to indigenous microorganisms. If leached cyanide levels do not become sufficiently low to permit biodegradation, cyanide could enter into the ground water. The extent of contamination would depend on the degradative capability of the extant population of microorganisms. Microbial degradation of cyanide under anaerobic conditions, however, is considered to be more sensitive to cyanide concentration than microbial degradation in aerated soil layers.

The environmental fate and transport of cyanides in mining wastes is summarized in Table 2-19. Specific technical points regarding the persistence and mobilization of cyanides in mining wastes are:

- Free cyanide and most forms of complexed cyanides are not generally persistent in the environment, although some sparingly soluble cyanide complexes of iron, cobalt, copper, and nickel decompose very slowly in solid wastes and aquatic sediment with concomitant release of cyanide ion.

- Free cyanide is volatile (as hydrogen cyanide) from aqueous solutions and is also subject to biodegradation at low concentrations. Complexed cyanides degrade at varying rates with the release of cyanide ion, but this degradation would be impeded by relatively large concentrations of free cyanide. Therefore, cyanides seem very persistent under conditions in which they are compartmentalized, such as in tailings sediments and the interior of compacted old waste piles. It is lack of physical mixing with other parts of the environment that exerts the greatest effect on persistence of free cyanides and metallocyanide complexes.

- Environmental conditions most conducive to rapid, natural destruction of cyanides in mining wastes would be aeration, intermittent rainfall, and neutralization of alkaline pH values by absorption of carbon dioxide.

- Secondary mobilization of complexed cyanides would be most affected by mechanical dissipation of material in which they are concentrated (e.g., tailings sediments and old waste piles). Heavy rainfall and flooding could transport both readily soluble and sparingly soluble complexed cyanides.

105

- Degradation of complexed cyanides with release of cyanide ion is increased by higher temperatures, and should also be increased by removal of cyanide ion. Both alkaline and acidic conditions can enhance the release of cyanide ion from metallocyanide complexes.

# 3. ACID GENERATING WASTES

This chapter presents a review of available data on quantities of metals mining and beneficiation wastes (cumulative, generated annually, and projected future generation) that have the potential for acid generation. To the extent possible with available data, waste volumes are estimated along with the total maximum acidity that may potentially be released from these wastes. Factors determining the rate of acid generation and release are discussed, and methods of estimating release rates are outlined. The data requirements for these methods are identified.

## 3.1 Identification of Acid Generating Mine Wastes

Acids are generated in metals mining and beneficiation wastes through the oxidation of base metal sulfides contained in these materials. Acid generation is initiated upon exposure of these sulfidic minerals to air and moisture during mining activities. Base metal sulfides most commonly associated with metal bearing ores are listed in Table 3-1. Of these, the most widely distributed mineral and the predominant source of acidity in most ores is iron pyrite (Ridge 1970). For this reason, acid generating sulfidic minerals are commonly referred to collectively as pyrite, and the acid generation potential of sulfidic ores is usually assessed based on pyrite content.

The chemistry of pyrite oxidation is complex and not thoroughly understood (Jaynes et al. 1984a). Acid generation probably occurs via several mechanisms, depending on conditions. The overall stoichiometry of the reactions, however, can be represented by the following equations:

$$FeS_2 + 3.5\ O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{\ 2-} + 2H^+ \qquad (1)$$

$$14\ Fe^{2+} + 3.5\ O_2 + 14\ H^+ \rightarrow 14\ Fe^{3+} + 7\ H_2O \qquad (2)$$

$$Fe^{+3} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (3)$$

$$FeS_2 + 14\ Fe^{+3} + 8\ H_2O \rightarrow 15\ Fe^{+2} + 2\ SO_4^{\ 2-} + 16\ H^+ \qquad (4)$$

Table 3-1. Sulfidic Minerals That Oxidize to Form Sulfuric Acid

| Mineral | Oxidation products |
|---|---|
| Pyrite, $FeS_2$<br>($FeS_2$ also occurs in another crystalline form, termed marcasite, usually at greater ore depths) | $FeSO_4$, $Fe_2(SO_4)_3$, $H_2SO_4$ |
| Molybdenite, $MoS_2$ | $MoO_3$, $H_2SO_4$ |
| Arsenopyrite, $FeAsS_2$ | $As_2O_3$, $FeSO_4$, $H_2SO_4$ |
| Cuproarsenopyrite, $CuAsS_2$ | $As_2O_3$, $CuSO_4$, $H_2SO_4$ |
| Realgar, $AsS_2$ | $As_2O_3$, $H_2SO_4$ |
| Stibnite $Sb_2S_3$ | $Sb_2O_3$, $H_2SO_4$ |
| Pyrrhotite ($FeS$) | $FeSO_4 \rightarrow Fe(OH)_3 + H_2SO_4$* |
| Chalcopyrite ($CuFeS_2$) | $CuSO_4$, $FeSO_4 \rightarrow Fe(OH)_3 + H_2SO_4$* |

*Sulfuric acid may be formed as a result of secondary oxidation.

The direct oxidation of iron disulfide (pyrite) by reaction with oxygen (Equation 1) results in the formation of two equivalents of acid per molecule of original pyrite. The ferrous iron thus liberated undergoes oxidation to ferric iron, and subsequently precipitates as the hydroxide (Equations 2 and 3), resulting in the net production of two additional acid equivalents. Hence, if all reactions go to completion four equivalents of acid are generated from a single molecule of pyrite (Burt 1981; Carrucio n.d.).

A second route of pyrite oxidation, through reaction with the ferric ion, is represented by Equation 4. This reaction is limited in most systems by the relatively slow rate of ferrous-to-ferric iron oxidation (Equation 2), and the availability of ferric iron in many systems. However, certain bacteria (Thiobacillus ferrooxidans) are known to greatly increase the rate of ferrous iron oxidation, and thereby to catalyze pyrite oxidation by the latter mechanism listed (Equation 4).

Assuming the production of four equivalents of acidity per molecule of pyrite, the stoichiometry of the oxidation reactions and atomic weights of involved elements indicate that one molecule of pyrite generates 1.67 equivalents of acid expressed as calcium carbonate ($CaCO_3$). This relationship forms the basis of acid-base accounting and of estimating maximum potential acidity of ore bodies, as detailed in subsequent sections.

Metal bearing ores which potentially contain pyritic minerals and which are mined in significant quantities in the United States are copper, lead, zinc, gold, and silver. The association of these metal ores with pyrites allows identification of wastes with acid-generating potential through identification of wastes generated by these mining and beneficiation segments nationwide. Three categories of waste materials must be considered in assessing potential acid-generating wastes: mine development wastes, tailings from milling processes (including vat leaching and beneficiation), and wastes from the dump leaching of low grade copper ores.

### 3.1.1 Mine Development Wastes

These wastes are generated by the excavation and construction operations undertaken to gain access to the ore body of interest. They include soils, overburden, rock, and subgrade ore containing metal of little economic value. Large amounts of mine development wastes are generated by open pit mining, while those generated by underground mining are of considerably lower volume relative to the volume of ore produced (Coppa 1984). Mine development waste materials vary widely in physical characteristics and mineralization; in some cases their mineralization bears no resemblance to that of the underlying ore body (Ridge 1970).

Mine development wastes are generally disposed of in waste piles near the mining site (Coppa 1984). When such materials contain pyrites and generate acids, two significant mechanisms of acid release to the environment are seepage (leaching of acids by moisture flux through the waste), and runoff (i.e., dissolution of acid into and transport of acid with runoff from the waste pile (Harries and Ritchie 1983)). Even where the associated ore body is known to contain high levels of pyrite, the potential for acid generation represented by mine development wastes is extremely difficult to assess. This is because of two factors: (1) mine development wastes range in physical form from fine material to large rocks, and the degree of disturbance or breakup of these wastes (and therefore internal oxygen and moisture availability) has a large effect on acid generation (Coppa 1984); and (2) pyrite content of overburden is usually very different from that of the ore body, and is unquantified in the reviewed literature. While in some cases mine development wastes are related geologically to those of the ore body, it is often the case that overburden material is from a different geologic formation than the ore body itself.

### 3.1.2 Milling Wastes (Tailings)

A portion of ore material removed from a mine is subjected to a physical and/or chemical beneficiation process near the mine site for the purpose of concentrating the metal values and separating them from the worthless ore material or gangue. Beneficiation includes crushing and grinding the ore to a fine particle size, and mixing of the crushed ore with water, forming a slurry in which the separation of values and gangue is accomplished. This separation is effected through physical settling, or through addition of chemical reagents that suppress gangue material and enhance the adherence to air bubbles and floatation of metal values. Residue from beneficiation, or tailings, is in the form of a slurry and contains most of the pyritic material that was in the original ore (Coppa 1984).

The vat leaching of ores is a second source of waste tailings. This process also involves crushing and grinding of ores to a fine particle size, and formation of a water slurry. The slurry is then leached with a strong reagent that dissolves the metal values. Reagents used include alkaline cyanide solutions (for leaching silver and gold), and strong acid solutions (vat-leaching of copper). The leach solution containing dissolved metal values is drained or decanted from the slurry and transferred to a metal recovery plant. The leached ore residue or tailings are disposed.

Tailings are usually pumped to an impoundment or pond for final disposal (Coppa 1984). Potential mechanisms of gradual or intermittent acid release from tailings ponds include: seepage of acidic leachate through pond liners or underlying soil, and overflow of acidic pond waters during storm events. Failure of retaining dikes or dams constitutes a potential mechanism of sudden, large-scale (catastrophic) acid release. The acidity of tailings may be similar to that of the original ore milled but, especially in the case of vat leaching, may be strongly influenced by the milling process used.

### 3.1.3 Copper Dump Leach Wastes

At many copper mining sites, waste material containing copper at levels too low for profitable handling by beneficiation, or entire mine ore production at sites where only low-grade ore is being mined, is placed in a dump area. These dump materials are leached with a dilute acid solution delivered to the top of the dump by a sprinkler system (See Figure 3-1). The acidic solution dissolves copper in the dump material, and copper bearing leachate (termed pregnant liquor) is collected at the foot of the dump for transfer to a holding pond and eventually to a copper recovery plant. Following recovery of copper from the pregnant liquor (usually by the processes of solvent extraction/ electrowinning or cementation), the acid solution, now essentially devoid of copper (termed barren solution), is transferred to a second holding pond. Solution in the barren solution holding pond is maintained at the desirable pH through addition of makeup water or acid, and is pumped from this pond to the top of the dump for reintroduction to the dump as leaching solution (Sheffer and Evans 1968).

A major waste resulting from copper dump leaching is the spent leach dump material. When the copper content of pregnant liquor recovered from a dump is below that which can be profitably extracted, and the dump leach operation is shut down, dump materials are left in place. Potential mechanisms for acid release from abandoned dumps include acid dissolution into and removal by rain water percolating through the dump, and acid dissolution into and removal by runoff from the dump. As most dump sites are selected for relatively impermeable surfaces and sloping topography in order to maximize recovery of pregnant liquor during operation, acid leachate produced by rain water percolation through abandoned dumps may be released to surface waters because of seepage from the foot of the dump pile to the surrounding soil surface, as well as to ground water through seepage through underlying soils.

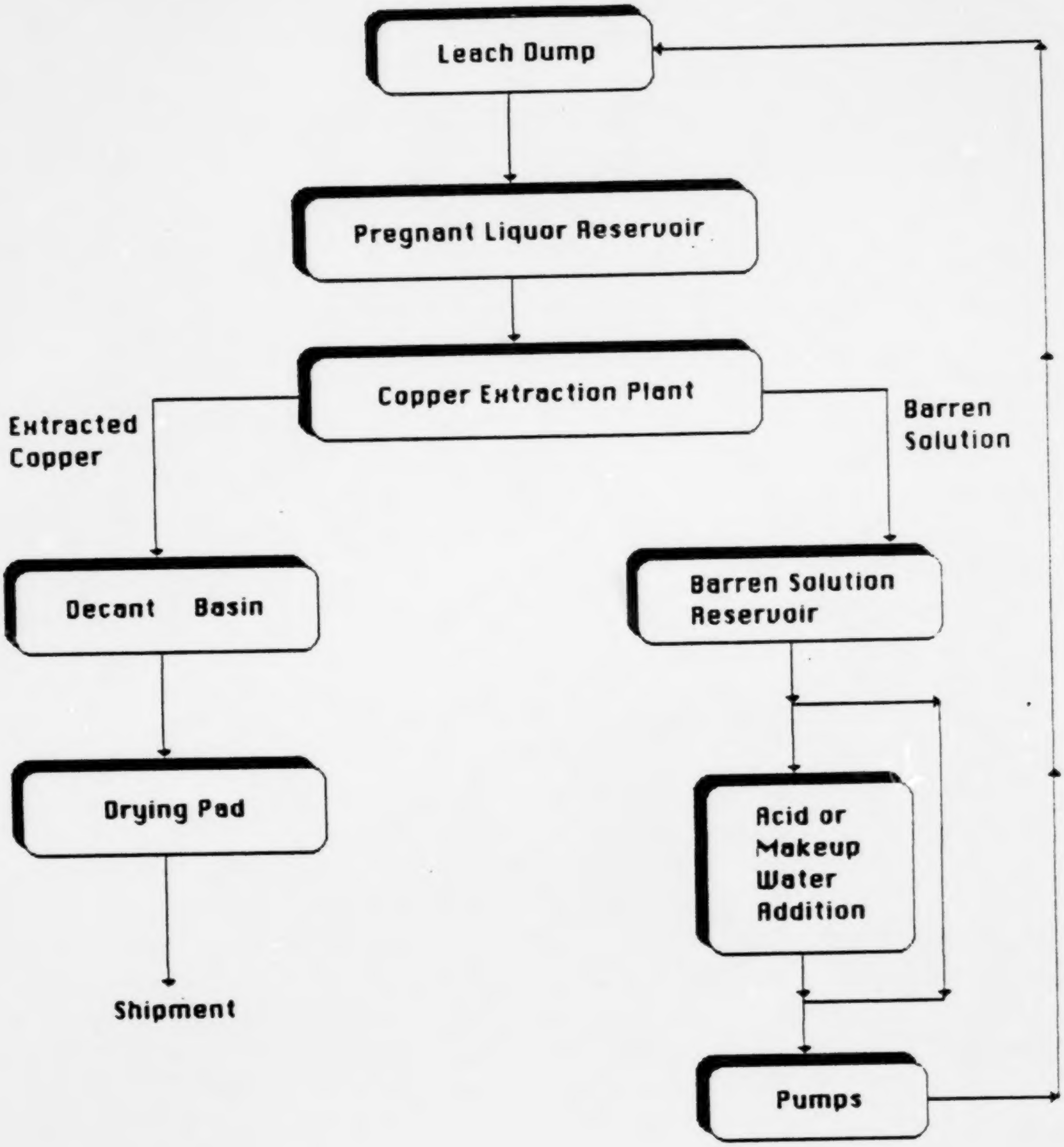

Leach Dump
Pregnant Liquor Reservoir
Copper Extraction Plant
Extracted Copper
Barren Solution
Decant Basin
Barren Solution Reservoir
Drying Pad
Acid or Makeup Water Addition
Shipment
Pumps

Figure 3.1 Generalized Flowsheet for Copper Dump Leaching Operations

Significant potential for acid release to the environment also exists during active operation of dump leach sites. Potential gradual or intermittent release mechanisms include: seepage of pregnant liquor through soils beneath the dump to ground water; seepage or leakage of acid solutions through soils or liners beneath solution holding ponds and transfer channels; and pond overflow or solution discharge caused by excessive liquid entering the solution cycle during storm events. Potential mechanisms of catastrophic releases during operation include the failure of leach liquor holding pond dams or liners.

As a final point regarding the identification of wastes with acid generation potential, this report does not focus only on those wastes that exhibit a pH less than or equal to 2.0 (the RCRA definition of corrosive hazardous wastes), or that generate waste waters exhibiting this pH level. Considerable evidence indicates that acidic waters exhibiting substantially higher pH levels have both direct and indirect impacts on human health and the environment. In summarizing the effects on aquatic ecosystems and biota of pH fluctuations or reduction in natural waters, Potter et. al. (1982) show that under neutral or slightly basic pH conditions, a fluctuation of 0.5 pH units results in significant ecosystem changes. Ecotoxic effects become increasingly pronounced with decreasing average pH or larger pH fluctuations. At a pH level of 3.5 or below, aquatic vertebrates and many other biotic species are eliminated.

Perhaps the most significant indirect impact on human health and the environment resulting from acidification of natural systems is the increase in solubility and bioavailability of toxic metals in water at reduced pH levels. At pH levels of 5.0 and below, soluble species of arsenic predominate under most redox conditions in natural waters. The reduction of pH levels to below 4.5 greatly increases the concentration of soluble species of both mercury and trivalent chromium in equilibrium with the insoluble hydroxide and oxide species. At pH levels of 6.0 or lower, the rate of adsorption of lead and copper to bed sediments greatly decreases, resulting in the increased release of soluble forms of these metals to the water column (Callahan et al. 1969).

Figure 3-2 illustrates the effect on the solubility of various metals of a pH reduction from 7.0 to 4.0. This figure is a simplification of the behavior of metals in natural waters, where metal solubility is also strongly influenced by temperature, the presence of other ions, and the water column redox potential. However, it does provide some indication of the effect of moderately acid pH levels on metal mobility.

It can be concluded that acids generated by metals mining and beneficiation wastes will have the effect of solubilizing and carrying into the ambient environment otherwise inert toxic metals present in these wastes. Numerous assays have indicated the commonly significant concentrations of heavy metals in mine wastes (e.g., PEI 1983; ERCO 1984).

As will be explained in subsequent sections, the exact pH of leachate or runoff from pyritic mine wastes is quantifiable only through site-specific waste testing or modeling; general data available in the reviewed literature allow only a semi-quantification of the maximum potential acidity available in such wastes. However, the foregoing demonstrates that any indication of acid generation potential for a waste material can be interpreted as an indication of potential for hazard to human health and the environment.

## 3.2 Mine Waste Volumes and Qualitative Assessment of Acid Generation Potential

### 3.2.1 Mine Development Wastes

(1) Volumes. The volumes of non-ore waste materials moved by the mining segments potentially associated with pyritic ore deposits are presented in the Minerals Yearbook (USBM, various years). These data are available only in aggregate for each commodity, and nationwide for each

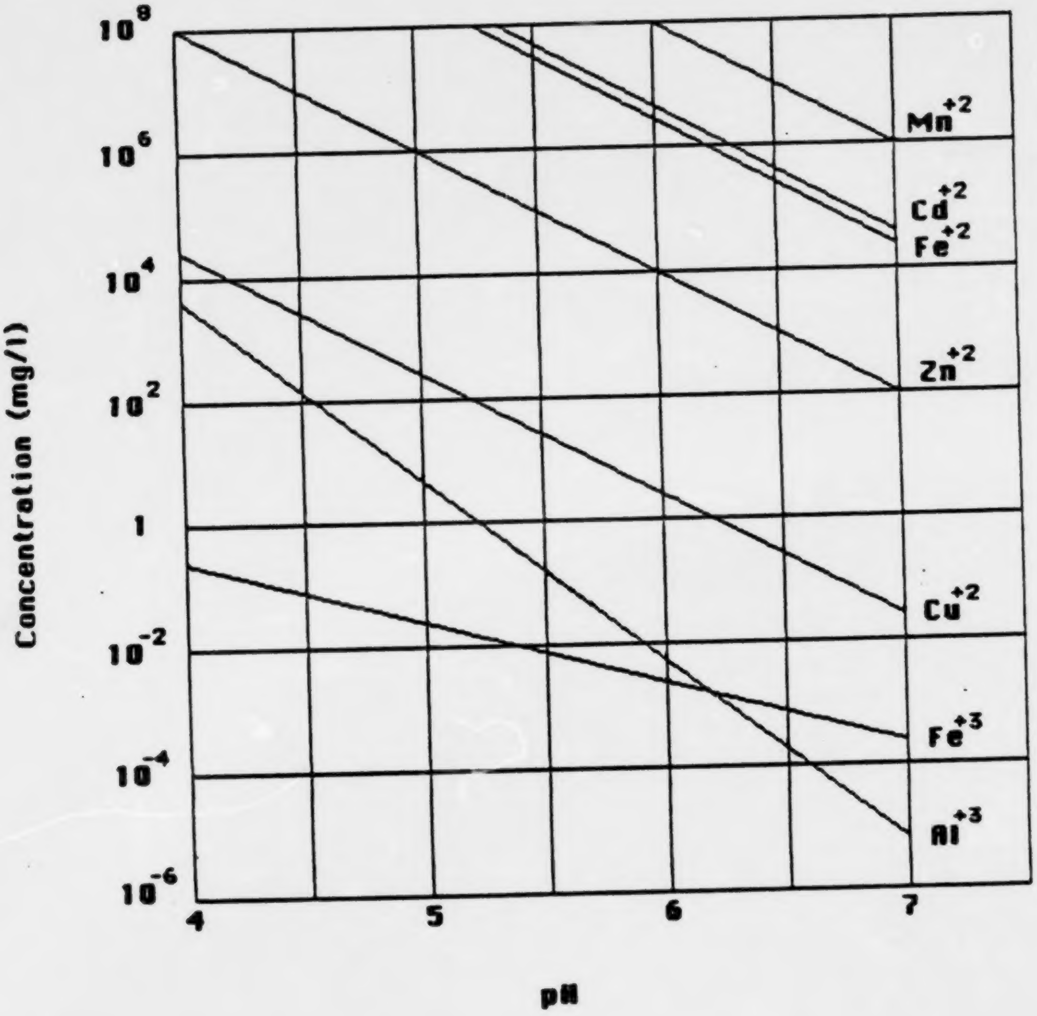


Figure 3-2 Solubilities of Oxides and Hydroxides of Various Metals (Stumm and Morgan 1970, as Presented in Martin and Mills 1976)

116

year beginning in 1974. Table 3-2 presents the total volumes generated between 1974 and 1983, and the ratios of wastes to crude ores generated for each year and commodity. These data indicate that current (1983) annual mines development wastes for the commodities of concern total approximately 317 million metric tons.

These data illustrate the significant disparity in waste-to-ore ratios among surface and subsurface mining operations. This ratio is considerably lower for the lead and zinc mining segments, which consist predominately of subsurface mines, than for the copper, gold, and silver segments in which open pit mining is more common (Coppa 1984).

The tabulated waste-to-ore ratios provide a means of roughly assessing the volumes of waste generated in years prior to 1979 when compared to volumes of ore produced in earlier years (as presented in the following section). However, such an assessment is rough at best because of the fluctuation in waste-to-ore ratios over the years for which these ratios are available. The fluctuation in this ratio reflects changing economic conditions, and the relative profitability of working lower grade ores (Coppa 1984).

(2) Acid generation potential. The potential of mine development wastes for acid generation represents one of the significant gaps in data required to assess nationwide acid generation from metals mining and benefication wastes. As stated earlier, mine development wastes cannot be expected to exhibit the same mineralization as associated ore bodies; often an oxidized layer of overburden and ore is found above a highly sulfidic ore body (Ridge 1970). While comprehensive treatises are available regarding the mineralization of ore bodies, no such comprehensive data were identified in the reviewed literature for mine development wastes. Information on mine development wastes may be available for individual mine sites from mining company data, journal articles, or pyritic alteration texts. While access and in-depth review of these potential sources were beyond the resources of the present project, some partial information regarding pyrite content of mine development wastes may possibly be developed in this manner in a future effort.

0697E

Table 3-2. Mine Development Waste and Waste to Ore Ratios for Mining Segments Commonly Associated with Pyritic Ores (Thousands of Metric Tons)

| | 1978 | | | 1979 | | | 1980 | | | 1981 | | | 1982 | | | 1983 | | | 1978-1983 Total | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Crude Ore | Waste | Waste/ Ore | Crude Ore | Waste | Waste/ Ore | Crude Ore | Waste | Waste/ Ore | Crude Ore | Waste | Waste/ Ore | Crude Ore | Waste | Waste/ Ore | Crude Ore | Waste | Waste/ Ore | Crude Ore | Waste | Avg. Waste/ Ore ratio |
| Cu | 237,634 | 342,846 | 1.44 | 251,239 | 497,036 | 1.98 | 217,680 | 481,617 | 2.21 | 276,635 | 599,527 | 2.17 | 177,772 | 323,799 | 1.82 | 177,772 | 234,006 | 1.32 | 1,338,732 | 2,460,831 | 1.84 |
| Pb | 8,689 | 2,059 | 0.24 | 8,907 | 2,195 | 0.25 | 9,796 | 2,594 | 0.26 | 8,753 | 2,023 | 0.23 | 8,771 | 1,859 | 0.21 | 7,627 | 2,059 | 0.27 | 53,543 | 12,789 | 0.24 |
| Zn | 5,805 | 1,152 | 0.20 | 5,025 | 1,642 | 0.33 | 6,458 | 1,088 | 0.17 | 6,440 | 762 | 0.12 | 5,841 | 1,043 | 0.18 | 5,170 | 513 | 0.10 | 34,019 | 6,200 | 0.18 |
| Ag | 1,669 | 1,823 | 1.09 | 1,814 | 714 | 0.39 | 1,796 | 6,013 | 3.35 | 5,016 | 11,610 | 2.31 | 6,077 | 19,954 | 3.28 | 8,577 | 6,829 | 0.80 | 24,949 | 46,943 | 1.88 |
| Au | 2,884 | 10,521 | 3.65 | 3,238 | 7,392 | 2.28 | 8,880 | 9,342 | 1.05 | 9,886 | 24,308 | 2.46 | 23,673 | 49,159 | 2.08 | 28,843 | 73,104 | 2.53 | 77,404 | 173,826 | 2.25 |

Source: U.S.B.M Minerals Yearbook, various years.

An additional data deficiency for assessing acid generation from these wastes is the degree of aggregation of available volume data (Table 3-2). Because mineral content is a localized phenomenon, mine development waste volumes disaggregated to the county or individual mine level would be required in order to utilize any mineralization data developed. As stated earlier, data are not available at this level of disaggregation.

A nationwide assessment of the acid generation potential of mine development wastes is, therefore, not feasible with data identified in the reviewed literature and through contacts with field experts during this project.

### 3.2.2 Tailings from Ore Beneficiation

(1) Volumes. A recent study (Coppa 1984) presents data allowing calculation of the quantities of ore processed by vat leaching and ore beneficiation mills* nationwide between the years 1910 and 1981. Data are broken down in this study by decade and on a county basis. All ores from copper, lead, zinc, gold, or silver mines in each county are combined to a single volume figure for each decade and county. Data regarding tons of ore processed, as adapted from Coppa (1984), are presented in Table 3-3.** Data are for all ores milled by the indicated mining segments, and the portions considered to have acid generation potential are tabulated. While the amount of pyrite remaining

---

*Personal communication with Luis Coppa, U.S. Bureau of Mines, December 12, 1985.

**These data have been calculated from data quantifying volumes of mine openings presented by Coppa (1984). The specific gravity for ore used by Coppa (personal communication, December 12, 1985) in calculating volumes from tons of ore processed is 2.6. This factor was employed in back calculating from volumes to tons of ore for the present report. The full conversion factors, after factoring in the weight-to-volume ratio of water, and the conversion from short tons to metric tons is: metric tons of ore = 1.99 x $yd^3$ of ore (personal communication with Luis Coppa, December 12, 1985). These and all data from the Coppa (1984) report must be regarded as approximate.

Table 3-3. Tons of Copper, Lead, Zinc, Gold Ore Concentrated or Vat Leached from 1910 to 1981; Source; Mineralization; and Acid Generation Potential

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| Arizona | Cochise | Central AZ Copperbelt | Cu | 103,100 | 0.2 to 8.0% | Highly variable | Ore body is complex, one copper mine accounts for most of waste | Intermediate |
| | Coconino | NA | Cu | 649 | NA | NA | Small copper deposit operated only in 1950s | - |
| | Gila | Banner central AZ Copperbelt | Cu-Mo | 597,900 | 0.2 to 8.0% | Negligible in central ore body, minor constituent at edges (up to 20%) | Ore body is complex consisting of an oxidated upper zone. Ore body occurs as large lenses in a partially dolomitic host formation | Intermediate |
| | Graham | Banner central AZ Copperbelt | Cu-Mo | 473 | " | " | | |
| | Greenlee | Banner central AZ Copperbelt | Cu-Mo | 624,200 | " | " | | |
| | Maricopa | NA | Au | 540 | NA | NA | Small, older gold mines | - |
| | Mojave | Mojave | Cu-Mo | 95,060 | Nil to over 5% | Negligible | Ore body consists of oxidized and sulfide-rich zones | High |
| | Pima | Banner central AZ Copperbelt | Cu-Mo | 1,276,000 | 0.2 to 8.0% | Negligible in central ore body, minor constituent at edges (up to 20%) | Same as Gila County | Intermediate |
| | Panal | Banner central AZ Copperbelt | Cu-Mo | 647,900 | " | | " | |
| | Santa Cruz | NA | Cu-Pb-Zn | 2,034 | NA | NA | Early small operations | - |
| | Yavapai | Bagdad | Cu-Mo | 125,400 | <1 | Negligible | Molybdenite also present | Intermediate |
| | Yuma | NA | Au-Cu-Pb | 1,182 | NA | NA | Mostly small older mines | - |
| Total ore processed | | | | 3,349,038 | | | | |
| Ore with intermediate acid generation potential | | | | 1,977,000 | | | | |
| Ore with high acid generation potential | | | | 95,060 | | | | |

Table 3-3. (continued)

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| California | Alpine | Zaca mine[e] | Ag/Zn | 24 | Significant[e] | Nil[e] | Elemental sulfur was also produced | |
| | Amador | Mother Lode[e] | Au | 11,430 | 1-4%[e] | Nil[e] | Gold mining ceased 1942 | High |
| | Butte | Mother Lode[e] | Au | 314 | 1.2%[e] | NA | - | - |
| | Calaveras | Mother Lode[e] | Au, Cu | 8,905 | 2-4%[e] | Nil[e] | Gold mining ceased 1942, may reopen | High |
| | El Dorado | Mother Lode[e] | Au | 1,255 | 1-4%[e] | Nil[e] | - | High |
| | Humboldt | NA | Cu/Zn | 42 | NA | Nil | Produced 1950s only | - |
| | Imperial | Pichacho[h] | Au | 211 | NA | NA | - | - |
| | Inyo | Darwin, Pine Creek[h] | Cu, W, Pb | 5,474 | Trace[h] | Major constituent[h] | - | Low |
| | Kern | NA | Au | 4,712 | NA | NA - | Mine closed 1930s | - |
| | Los Angeles | NA | Au/Ag | 171 | NA | NA | - | - |
| | Madera | NA | Au | 50 | NA | NA | - | - |
| | Mariposa | Mother Lode[e] | Au | 1,176 | 2-4%[e] | Trace[e] | - | Intermediate |
| | Mono | Bodie[h] | Au, Ag | 945 | Trace | Major constituent[h] | Mine closed 1915 | Low |
| | Napa | NA | Ag, Hg | 99 | NA | NA | - | - |
| | Nevada | Mother Lode[e] | Au | 13,034 | 1-2%[e] | NA | Mines closed 1956 | - |
| | Placer | Mother Lode[e] | Au | 715 | 1-2%[e] | NA | - | - |
| | Plumas | Gennessee Copper Belt[h] | Cu/Au | 9,370 | 2-4%[h] | Nil | Mines closed 1920s; may reopen | High |
| | Riverside | NA | Au Pb | 44 | NA | NA | - | - |
| | San Bernardino | Randsburry[h] | Au/Ag | 755 | NA | NA | - | - |
| | Shasta | Shasta/Trinity[h] | Cu Zn Au, pyrite | 3,242 | Over 10%[h] | Nil[h] | Operations ceased before 1950 | High |
| | Sierra | Mother Lode[e] | Au | 1,704 | 1-2%[e] | Nil[e] | | High |
| | Siskiyou | Collahon/Deadwind[h] | Au/Ag | 1,222 | NA | NA | - | - |
| | Trinity | Shasta/Trinity[h] | Au | 207 | Up to 10%[h] | Nil[h] | - | High |
| | Tuolumne | Mother Lode[e] | Au | 2,817 | 2-4%[e] | Trace[e] | Gold mining stopped 1930s | Intermediate |
| | Yuba | Mother Lode[e] | Au | 119 | 1-2%[e] | Trace[e] | | Intermediate |
| Total ore processed | | | | 68,037 | | | | |
| Ore with high acid generation potential | | | | 35,906 | | | | |
| Ore with intermediate acid generation potential | | | | 4,112 | | | | |

Table 3-3. (continued)

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| Colorado | Boulder | NA | Au/Ag | 969 | NA | NA | – | |
| | Chaffee | NA | Zn | 262 | NA | NA | Pre-1950s | |
| | Clear Creek | NA | Cu/Au/Ag | 12,590 | Present | Nil | Old gold district | Intermediate |
| | Conejos | NA | Ag/Au | 34 | NA | NA | – | |
| | Custer | NA | Au/Ag | 270 | NA | NA | – | |
| | Dolores | Puzzler mine[f] | Zn Pb Cu Ag | 1,110 | 8%[f] | NA | Other sulfides 14% | |
| | Eagle | Gilman | Zn | 8,658 | Over 30% | Negligible | | High |
| | Gilpin | Gilman | Au Ag | 1,903 | Over 30% | Negligible | | High |
| | Gunnison | NA | Zn Pb Ag | 699 | NA | NA | | |
| | Lake | Leadville | Zn Pb Ag | 6,630 | 11-14% | 50%[g] | Major Pb/Zn district | Low |
| | Mineral | | Ag | 2,590 | NA | NA | | |
| | Ouray | San Juan | Zn Pb Ag | 4,263 | Highly variable | Negligible | Also some of Au mines | Intermediate |
| | Park | NA | Pb/Ag | 1,234 | NA | NA | | |
| | Pitkin | NA | Pb/Ag | 1,303 | NA | NA | | |
| | Rio Grande | NA | Au | 288 | NA | NA | | |
| | Saguache | NA | Ag | 606 | NA | NA | | |
| | San Juan | San Juan | Zn Pb Ag | 10,680 | Highly variable | Nil | | Intermediate |
| | San Miguel | San Juan | Zn/Pb/Cu/Ag | 18,930 | Highly variable | Nil | | Intermediate |
| | Summit | Climax | Ag/Pb/Zn/Mo | 1,255 | 2-3% | Negligible | Major Mo district | High |
| | Teller | Cripple Creek | Au | 18,560 | Variable | Negligible | Mostly pre-1930 | Intermediate |
| Total ore processed | | | | 92,834 | | | | |
| Ores with high acid generation potential | | | | 11,816 | | | | |
| Ores with intermediate acid generation potential | | | | 65,023 | | | | |

Table 3-3. (continued)

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| Idaho | Adams | 7 Devils | Cu/Ag | 777 | Trace | Significant, levels of limestone in host rock | Mostly pre-1950 production | Low |
| | Blaine | NA | Ag, Pb, Zn | 1,996 | NA | NA | – | |
| | Boise | NA | Au/Ag | 648 | NA | NA | – | |
| | Bonner | NA | Au/Ag | 397 | NA | NA | – | |
| | Boundary | NA | Au/Ag | 576 | NA | NA | – | |
| | Butte | NA | Au | 62 | NA | NA | Pre-1950 production | |
| | Custer | Phi Kappa Mine | Ag, Pb, An[f] | 2,509 | 1%[f] | 0.005%[f] | Other sulfides 1% | Intermediate |
| | Elmore | NA | Au/Ag | 886 | NA | NA | – | |
| | Fremont | NA | Au/Ag | 44 | NA | NA | Mostly pre-1950 production | |
| | Idaho | NA | Au | 495 | NA | NA | Mostly pre-1950 production | |
| | Lemhi | NA | Au | 2,866 | NA | NA | Mostly pre-1950 production | |
| | Owyhee | Silver City | Au/Ag | 3,264 | Present | Nil | Reactivated old Silver District | Intermediate |
| | Shoshone | Coeur d'Alene | Pb/Zn/Ag | 108,500 | 1->3 | Nil to several % | Arsenopyrite also present | Intermediate |
| | Valley | Blackbird | Ag | 4,064 | Significant | Nil | Ore is sulfide based in silicate matrix | Intermediate |
| | Washington | Bayhorse | Pb/Zn/Ag | 4,271 | Trace | Significant | Ore is carbonate based | Low |
| Total ore processed | | | | 131,355 | | | | |
| Ore with intermediate acid generation potential | | | | 118,377 | | | | |
| Illinois | Hardin | Ill-Ky Zinc Belt | Zn, fluorite lead, barite | 8,126 | 0.001% | 57.5% | | Low |
| | Jo Daviess | " | " | 10,430 | 0.001% | 57.5% | | Low |
| Total ore processed | | | | 18,556 | | | | |
| Kansas | Cherokee | Tri State Zn district | Pb/Zn | 105,000 | 0.5% | Major constituent >50% | – | Low |

123

Table 3-3. (continued)

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| Kentucky | Crittenden | Il-Ky Zn Belt | Pb/Zn | 328 | 0.001% | 57.5% | | Low |
| | Livingston | Il-Ky Zn Belt | | 1,541 | 0.001% | 57.5% | | Low |
| | Owen | Il-Ky Zn Belt | | 72 | 0.001% | 57.5% | | Low |
| Total ore processed | | | | 1,941 | | | | |
| Maine | Hancock | NA | Cu/Zn | 1,605 | Significant | Nil | - | Intermediate |
| Ore with intermediate acid generation potential | | | | 1,605 | | | | |
| Michigan | Houghton | White Pine Shale | Cu | 233,900 | 2-3% | 20-30% | Also contains up to 5% iron oxide | Low |
| | Keweenaw | White Pine Shale | Cu | 21,090 | 2-3% | 20-30% | Also contains up to 5% iron oxide | Low |
| | Ontonagon | White Pine | Cu | 132,400 | 2-3% | 20-30% | Also contains up to 5% iron oxide | Low |
| Total ore processed | | | | 387,390 | | | | |
| Missouri | Crawford | SE Mo Pb Belt | Pb, Zn | 7,453 | 8-10% | 80% | - | Low |
| | Iron | SE Mo Pb Belt | Pb, Zn, Fe | 43,600 | 8-10% | 80% | Silver is minor byproduct | Low |
| | Jasper | Tristate Zn Belt | Pb, Zn | 113,300 | 0.5% | > 50% | - | Low |
| | Jefferson | SE Mo Pb Belt | Pb, Zn | 155 | 8-10% | 80% | - | Low |
| | Lawrence | SE Mo Pb Belt | Pb, Zn | 814 | 8-10% | 80% | - | Low |
| | Madison | SE Mo Pb Belt | Pb, Zn | 26,460 | 8-10% | 80% | - | Low |
| | Moniteau | Tristate Zn Belt | Pb, Zn | 91 | 0.5% | > 50% | - | Low |
| | Newton | Tristate Zn Belt | Pb, Zn | 1,096 | 0.5% | > 50% | - | Low |
| | Reynolds | SE Mo Pb Belt | Pb, Zn | 37,800 | 8-10% | 80% | - | Low |
| | St. Francois | SE Mo Pb Belt | Pb, Zn | 241,500 | 8-10% | 80% | - | Low |
| | Washington | SE Mo Pb Belt | Pb, Zn | 23,920 | 8-10% | 80% | Also barite | Low |
| Total ore processed | | | | 496,189 | | | | |

Table 3-3. (continued)

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| Montana | Beaverhead | NA | Pb/Ag/Au | 377 | Significant[e] | Nil[e] | – | Intermediate |
| | Broadwater | NA | Pb/Au | 491 | NA | NA | – | – |
| | Cascade | Helena, Marysville | Cu/Pb | 1,656 | Trace | Major constituent | Host rock is dolomite | Low |
| | Chouteau | " | Au/Ag | 123 | NA | NA | – | – |
| | Deer Lodge | " | Au/Ag | 203 | up to 13%[e] | Nil[e] | – | High |
| | Fergus | " | Au/Ag | 806 | NA | NA | – | – |
| | Granite | Philipsburg | Ag/Zn | 1,108 | Trace | Major constituent | Host rock is dolomite | Low |
| | Jefferson | Philipsburg | Zn Pb Ag | 1,194 | NA | NA | – | |
| | Judity Basin | Philipsburg | Ag Pb Zn | 361 | NA | NA | – | |
| | Lewis & Clark | Philipsburg | Au/Ag | 2,548 | NA | NA | – | – |
| | Lincoln | Philipsburg | Ag/Cu | 1,106 | NA | NA | – | – |
| | Madison | Philipsburg | Ag/Cu | 1,150 | NA | NA | – | – |
| | Mineral | Coeur d'Alene | Ag | 312 | 1-3% | Nil to several % | Complex ore body | Intermediate |
| | Missoula | NA | Pb/Ag | 64 | NA | NA | – | |
| | Park | NA | Au | 1,152 | Present | Nil | – | Intermediate |
| | Phillips | Philipsburg | Au/Ag | 1,851 | Trace | Major constituent | Host rock is dolomite | Low |
| | Powell | Philipsburg | Au | 30 | NA | NA | – | – |
| | Sanders | Philipsburg | Pb/Zn | 463 | NA | NA | – | – |
| | Silver Bow | Butte | Cu, Zn, Mn | 474,200 | Up to 13% pyrite occurs in veins | 0-11% Calcite occurs primarily at boundaries of ore body. | $MoS_2$ also present | Intermediate |
| Total ore processed | | | | 489,195 | | | | |
| Ore with high acid generation potential | | | | 203 | | | | |
| Ore with intermediate acid generation potential | | | | 476,041 | | | | |

125

Table 3-3. (continued)

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| Nevada | Churchill | NA | Au | 707 | NA | NA | - | - |
| | Clark | NA | Au | 1,013 | NA | | | |
| | Elko | Mountain City Copper Dist. | Cu | 3,889 | NA | NA | Also some Au, Ag | - |
| | Esmeralda | Gabbs | Au | 5,654 | Trace | Major constituent | - | Low |
| | Eureka | Roberts Mountain | Au | 12,117 | Trace | 15-65% | | Low |
| | Humboldt | Battle Mountain[i] | Au | 4,967 | Up to 75% total sulfides | Nil | Pyrite is the major sulfide present | High |
| | Lander | Roberts Mountain | Au | 26,340 | Trace | 15-65% | - | Low |
| | Lincoln | Pioche | Au | 5,958 | 12-15% | Major constituent | Ore body has two zones, one carbonate rich, the other pyrite rich | Intermediate |
| | Lyon | Yerrington[j] | Cu | 126,900 | Minor constituent | Significant | Ore is oxide/carbonate based | Low |
| | Mineral | Yerrington[j] | Cu | 1,215 | Minor constituent | Significant | Ore is oxide/carbonate based | Low |
| | Nye | Gabbs | Au | 675 | Trace | Major constituent | - | Low |
| | Pershing | NA | Cu | 1,903 | NA | NA | - | - |
| | Storey | Comestock, VA City | Ag | 6,099 | Present | Nil | - | - |
| | Washoe | NA | Au | 111 | NA | NA | - | - |
| | White Pine | Ely | Cu | 302,500 | 0.2-1.0% | Variable but high at ore body edges | Ore body also has an oxidized zone containing little pyrite and a sulfide zinc zone with higher pyrite content | Intermediate |
| Total ore processed | | | | 500,048 | | | | |
| Ore with high acid generation potential | | | | 4,970 | | | | |
| Ore with intermediate acid generation potential | | | | 308,458 | | | | |
| New Jersey | Sussex | Franklin | Zn | 26,100 | Minor constituent | Major constituent | Ore is carbonate based. | Low |

1. 186

Table 3-3. (continued)

| State | County$^b$ | Ore body$^a$ | Minerals$^b$ mined | Ore milled (thousands of metric tons)$^c$ | Pyrite content (% $FeS_2$)$^d$ | Carbonate content (% as $CaCO_3$)$^d$ | Comments$^d$ | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| New Mexico | Catron | NA | Au/Ag | 751 | NA | NA | | |
| | Colfax | NA | Au/Ag | 135 | NA | NA | | |
| | Grant | Santa Rita/Tyrone | Cu/Zn | 502,300 | 0.03-2.0% | 1-3.4% | $MoS_2$ is also present (.007%) | Intermediate |
| | Hidalgo | Santa Rita/Tyrone | Cu | 2,592 | 0.03-2.0% | 1-3.4% | $MoS_2$ is also present (.007%) | Intermediate |
| | Lincoln | NA | Au/Ag | 44 | NA | NA | | |
| | Otero | NA | Au/Ag | 24 | NA | NA | | |
| | San Miguel | NA | Cu | 2,105 | NA | NA | | |
| | Sandoval | NA | Cu | 3,156 | NA | NA | | |
| | Santa Fe | NA | Au/Cu | 272 | NA | NA | | |
| | Socorro | NA | Au/Pb | 2,208 | NA | NA | | |
| Total ore processed | | | | 513,587 | | | | |
| Ore with intermediate acid generation potential | | | | 504,892 | | | | |
| New York | St. Lawrence | Balmat | Zn | 28,390 | 18.5% | 6.5% | | High |
| Ore with high acid generation potential | | | | 28,390 | | | | |
| North Carolina | Ashe | NA | Cu | 1,293 | 25-60% | Nil | Wastes are from the 1950s | High |
| | Catawba | NA | Au | 24 | NA | NA | Wastes are from pre-1920 | |
| | Montgomery | NA | Au | 79 | NA | NA | Wastes are from pre-1920 | |
| | Vance | NA | Cu | 550 | NA | NA | Wastes are from pre-1920 | |
| Total ore processed | | | | 1,946 | | | | |
| Ore with high acid generation potential | | | | 1,293 | | | | |

Table 3-3. (continued)

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| Oklahoma | Jackson | Tri state Pb-Zn | Pb/Zn | 1,517 | 0.5% | >50% | - | Low |
| | Ottawa | Tri state Pb-Zn | Pb/Zn | 256,100 | 0.5% | >50% | - | Low |
| Total ore processed | | | | 257,617 | | | | |
| Oregon | Baker | Iron Dyke Mine[f] | Cu | 1,470 | 4.0%[f] | Nil[f] | - | High |
| | Grant | NA | Au/Ag | 183 | NA | NA | Mostly pre-1930 operations | |
| | Jackson | NA | Au | 68 | NA | NA | Mostly pre-1930 operations | |
| | Josephine | NA | Au | 107 | NA | NA | Mostly pre-1930 operations | |
| | Lane | Champion Mine[f] | Au | 44 | 3.0%[f] | 15%[f] | Mostly pre-1930 operations | Low |
| | Malheur | NA | Au | 28 | NA | NA | Mostly pre-1930 operations | |
| Total ore processed | | | | 1,900 | | | | |
| Ore with high acid generation potential | | | | 1,470 | | | | |
| Pennsyl-vania | Lebanon | Cornwall | Zn/Cu/Fe | 56,030 | 2.5% | 0.01 to 39% | Pockets of limestone are present in the ore | Intermediate |
| | Lehigh | Friedensville | Zn | 7,056 | 0.63% | 0.01 to several % | | Intermediate |
| Total ore processed | | | | 63,068 | | | | |
| Ore with intermediate acid generation potential | | | | 63,068 | | | | |
| South Carolina | Lancaster | NA | Au | 512 | Present[f] | Nil[f] | Mining was primarily in 1930s | Intermediate |
| Ore with intermediate acid generation potential | | | | 512 | | | | |

Table 3-3. (continued)

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| South Dakota | Lawrence | Homestake | Au | 97,240 | 7-8% including arsenopyrite | Nil | Host rock is primarily quartz and other silicates | High |
| | Pennington | NA | Au | 171 | NA | NA | | |
| Totals ore processed | | | | 97,411 | | | | |
| Total ore with high acid generation potential | | | | 97,240 | | | | |
| Tenessee | Grainger | NA | Zn | 1,108 | NA | NA | | - |
| | Hancock | Jefferson City Zn Belt | Zn | 4,333 | < 1.0% | > 50% | Ore is carbonate based and contains dolomites | Low |
| | Jefferson | Jefferson City Zn Belt | Zn | 67,320 | < 1.0% | > 50% | Ore is carbonate based and contains dolomites | Low |
| | Knox | Jefferson City Zn Belt | Zn | 26,970 | < 1.0% | > 50% | Ore is carbonate based and contains dolomites | Low |
| | Polk | Copperhill | Zn, Cu, Fe | 57,230 | 49 to 63% | Minor (<20%) | Major product is iron ore | High |
| | Smith | Jefferson City Zn Belt | Zn | 3,538 | > 1% | > 50% | Same as for Hancock | Low |
| | Union | NA | Zn | 28 | NA | NA | | |
| | Washington | Jefferson City Zn Belt | Zn | 961 | < 1% | > 50% | Same as for Hancock | Low |
| Totals ore processed | | | | 161,488 | | | | |
| Ore with high acid generation potential | | | | 57,230 | | | | |
| Texas | Presidio | Terlingua[e] | Ag, Hg | 1,692 | Up to 5%[e] | Nil[e] | Mined prior to 1950 | Intermediate |
| Ore with intermediate acid generation potential | | | | 1,692 | | | | |

Table 3-3. (continued)

| State | County | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| Utah | Beaver | NA | Cu | 2,173 | NA | NA | NA | |
| | Box Elder | NA | Ag | 127 | NA | NA | | |
| | Grand | NA | Cu | 68 | NA | NA | | |
| | Juab | Tintic[k] | Pb/Zn/Ag | 1,206 | <3%[k] | 25%[k] | | Low |
| | Piute | NA | Au/Ag | 145 | NA | NA | | |
| | Salt Lake | Bingham Canyon | Cu/Zn/Ag | 1,381,000 | 1-75% | High to nil | Ore body is heterogenous, some areas are pyrite rich, others carbonate based | Intermediate |
| | San Juan | NA | Cu | 1,341 | NA | NA | NA | |
| | Summit | Dale City | Zn/Pb | 6,528 | Low | Major constituent | | Low |
| | Tooele | Bingham Canyon | Cu/Zn/Ag | 6,141 | 1-75% | High to nil | Same as for Salt Lake | Intermediate |
| | Utah | Tintik[k] | Pb/Zn/Au | 1,750 | >3%[k] | 25%[k] | | Low |
| | Wasatch | Park City | Cu/Pb/Zn | 5,340 | Low | Major constituent | | Low |
| Total ore processed | | | | 1,405,819 | | | | |
| Ore with intermediate acid generation potential | | | | 1,387,141 | | | | |
| Vermont | Orange | NA | Cu/Zn | 2,669 | Major constituent along with phyrrotite. | Trace to minor constituent. | - | Intermediate |
| Ore with intermediate acid generation potential | | | | 2,669 | | | | |
| Virginia | Orange | NA | Zn | 24 | NA | NA | - | - |
| | Rockingham | NA | Zn | 1,148 | NA | NA | - | - |
| | Wythe | Austinville | Zn | 25,800 | 0.6 to 3.4% | Present at significant levels | Ore body is nonhomogeneous | Intermediate |
| Total ore processed | | | | 26,972 | | | | |
| Ore with Intermediate acid generation potential | | | | 25,800 | | | | |

Table 3-3. (continued)

| State | County[b] | Ore body[a] | Minerals[b] mined | Ore milled (thousands of metric tons)[c] | Pyrite content (% $FeS_2$)[d] | Carbonate content (% as $CaCO_3$)[d] | Comments[d] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|
| Washington | Chelan | NA | Cu/Zn | 9,219 | NA | NA | Pre-1970 | |
| | Ferry | Republic | Au/Ag | 2,965 | Significant | Nil | | Intermediate |
| | Okanogan | NA | Ag | 218 | NA | NA | | - |
| | Pend Oreille | Metalaine | Pb/Zn | 17,460 | Highly variable | Present at edges of ore body. | Ore body is nonhomogeneous | Intermediate |
| | Snohomish | NA | Cu | 274 | NA | NA | Mined pre-1950 | - |
| | Stevens | Vanstone | Pb/Zn | 5,213 | High (>10%) | < 2% | | High |
| | Whatcom | NA | Au/Ag | 131 | NA | NA | | |
| Total ore processed | | | | 35,480 | | | | |
| Ore with high acid generation potential | | | | 5,213 | | | | |
| Ore with Intermediate acid generation potential | | | | 20,425 | | | | |
| Wisconsin | Grant | Upper Miss. Valley Dist. | Pb/Zn | 14,310 | 0.7 to 3.0% | Major constituent (>50%) | Mostly pre-1950 | Low |
| | Iowa | Upper Miss. Valley Dist. | Pb/Zn | 4,566 | 0.7 to 3.0% | Major constituent (>50%) | Mostly pre-1950 | Low |
| | Lafayette | Upper Miss. Valley Dist. | Pb/Zn | 23,020 | 0.7 to 3.0% | Major constituent (>50%) | Mostly pre-1950 | Low |
| Total ore processed | | | | 41,896 | | | | |
| National total ore processed | | | | 8,307,735 | | | | |
| National total ore with high acid generation potential | | | | 338,788 | | | | |
| National total ore with intermediate acid generation potential | | | | 4,949,777 | | | | |

Table 3-3. (Footnotes)

[a] Ridge 1970 unless otherwise specified.
[b] Coppa 1984.
[c] Calculated from Coppa (1984) data, using conversion factors provided by Luis Coppa (personal communication 12/12/85).
[d] Ridge (1970) unless otherwise specified.
[e] Newhouse (1969).
[f] U.S.B.M. Minerals Availability System Data Base.
[g] Carbonate data for a single mine only, Resurrection mine.
[h] USGS/CDMG/USBM 1966.
[i] Jackson 1982.
[j] Sheffer and Evans 1968.
[k] Nichols and Peterson 1970.

in tailings and going to disposal sites is directly related to the amount of ore processed, it may be of interest to note the tons of tailings produced in processing these ores. Coppa[*] states that the weight of tailings generated equals approximately 95 percent of ore weight; this factor can be applied to the data in Table 3-3 to assess tons of tailings present at mine operations as of 1981. This rough method of estimation does not take into account the tailings used in construction, road grading, or placed in precious metal heap leaching operations. Coppa (1984) states that a portion of tailings generated go to these uses rather than to disposal; this portion cannot be quantified with available data.

Data for volumes of ore processed during more recent years (1982 and 1983) are available in the Minerals Yearbook on a nationwide basis, by commodity. These data are presented in Table 3-4. Note that not all ores recorded in Table 3-4 contain pyrites; the portion containing pyrites can be estimated through application of the appropriate percent figures from Table 3-3. Amounts of lead and zinc ore milled could not be distinguished in Minerals Yearbook data from ore sent directly to smelters, and are therefore not avaiable.

(2) Acid generation potential.

Several sources of data are available that allow assessment of the acid generation potential of tailings produced from milling of metallic ores. The pyrite and carbonate contents of individual ore bodies are presented by Ridge (1970) and Newhouse (1969). The U.S. Bureau of Mines Minerals Availability System (MAS) data base contains mineralization data for numerous individual mines, and USGS/CDMG/USBM (1966) contains similar data for mineral resources of California. Table 3-3 presents the data regarding ore pyrite and carbonate contents for each county, as obtained from these sources. Although mineralization data are unavailable for

---

[*] Personal communication with Luis Coppa, U.S. Bureau of Mines, December 12, 1985.

133

Table 3-4. Ore Processed by Concentration and Vat Leaching for the Period 1982 Through 1984 (thousands of metric tons)

| | 1982 | 1983 | 1984 |
|---|---|---|---|
| Copper | 277,516 | 177,930 | 123,995 |
| Gold | 201,246 | 171,027 | 136,059. |
| Silver | 210,487 | 175,247 | 203,957 |

Source: Jolly and Edelstein 1984; Lucas 1985a; Reese 1985a.

numerous counties, those ores for which at least qualitative pyrite and carbonate contents are available represent approximately 99 percent of the total ores beneficiated by these mining segments.

Based on these mineralization data, a qualitative assessment of the acid generation potential of each ore body was made, the results of which are presented in Table 3-3. This assessment was performed by comparing the relative concentration of pyrites and carbonates in each ore after conversion of pyrite content to $CaCO_3$ equivalents. Four categories were developed into which ores were ranked:

- High potential for acid formation, where pyrite levels significantly exceed carbonate levels.
- Intermediate potential for acid formation, where pyrite and carbonate levels are comparable, or where ore bodies are highly nonhomogeneous with respect to pyrite or carbonate content.
- Low potential for acid formation, where carbonate levels significantly exceed those of pyrite.
- Unknown acid formation potential, where insufficient composition information is available to judge formation potentials. This category is indicated by a blank in that column of Table 3-3.

On this basis, it is estimated that approximately 5.3 billion metric tons of ore milled between 1910 and 1981 have either high or intermediate acid generation potential. This represents approximately 64 percent of all ores milled and tailings generated by the associated mining/beneficiation segments.

Figure 3-3 depicts amounts of cumulative milled ores (for the period 1910-1981) considered to have high or intermediate acid generation potential in each state, based on the data in Table 3-3 (from Coppa (1984); Ridge (1970); Newhouse (1969); and MAS). In the following subsections, a state-by-state assessment of ore bodies mined, mineralization, and acid generation potential as determined from these references is presented.

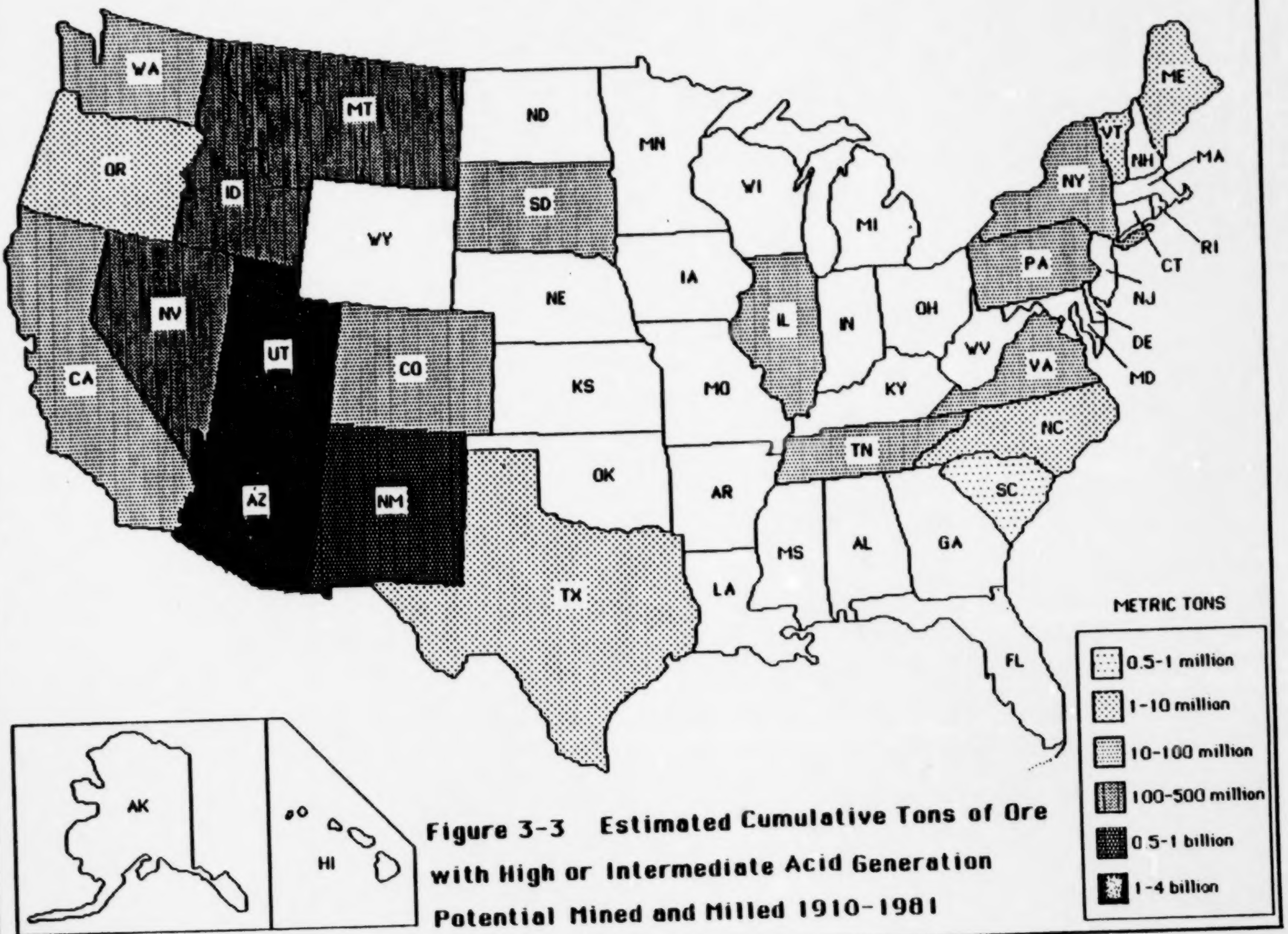

WA
OR
CA
NV
ID
MT
WY
UT
AZ
CO
NM
ND
SD
NE
KS
OK
TX
MN
IA
MO
AR
LA
WI
IL
MI
IN
OH
KY
TN
MS
AL
GA
FL
SC
NC
VA
WV
PA
NY
VT
NH
ME
MA
RI
CT
NJ
DE
MD
AK
HI
METRIC TONS
0.5-1 million
1-10 million
10-100 million
100-500 million
0.5-1 billion
1-4 billion

Figure 3-3 Estimated Cumulative Tons of Ore with High or Intermediate Acid Generation Potential Mined and Milled 1910-1981

(a) Arizona. Most of the ore production has been from the Central Arizona copperbelt, an area of southeastern Arizona with several overlapping ore bodies of very similar composition. These ore bodies generally consist of an upper oxidized, carbonate based zone and a lower, sulfide mineralized zone. Pyrite content ranges from 0.2 to 8.0 percent, with the highest usually near the surface and at the edges of the ore bodies. These ore bodies are worked primarily for copper, although lesser amounts of other metals have been or are being recovered. These ores generally also contain up to 0.5 percent molybdenite ($MOS_2$), (Ridge 1969). However, most facilities recover this material as a coproduct, so that little $MoS_2$ is to be expected in the tailings.

(b) California. Most ore production in California occurred prior to 1955, when the large gold mines in the Mother Lode belt closed. The old gold ores contained from 1 to 4 percent pyrite and negligible carbonate levels. The Mother Lode is again expected to become a significant mining area, however. According to the 1984 Minerals Yearbook, hundreds of old mines in the region are being evaluated for possible reopening. Ore compositions data could not be formed for a few small districts; however, these accounted for under 4 percent of waste generation.

(c) Colorado. Most ore production has been lead/zinc/silver production in still active major mining districts. Data could not be found for ore compositions for several small districts. However, these districts cumulatively generated only 10 percent of the wastes.

(d) Idaho. Most of the production has been from two sources - the Coeur D'Alene Pb/Zn/Ag district and from five other silver districts. Data on ore compositions could not be found for several small deposits that generated about 5 percent of the wastes.

(e) Illinois. All ore production has been from the zinc belt at the south end of the state, where ore compositions are known. Barite and fluorspar are produced as coproducts of the mining operations.

(f) Kansas. All production is from one county in the southeastern corner; the ore is carbonate based.

(g) Kentucky. All production is from the western portion of the state and ore compositions are known.

(h) Maine. All production is intermittent from one zinc and copper mine; the ore is pyritic.

(i) Michigan. All production is from one copper ore body of known composition.

(j) Missouri. All production is from two major lead-zinc ore bodies of known compositions.

(k) Montana. Most of the production has been from the Butte copper ore body, where zinc, lead, silver, and manganese are recovered as byproducts of copper mining. Information on ore compositions in several small districts could not be found. However, these districts account for only 2 percent of the wastes produced.

(l) Nevada. Most of the waste has been generated by two large copper mines. Ore composition information could not be found for a few small districts that account for about 1.5 percent of the wastes produced.

(m) New Jersey. All ore production has been from a single zinc mine that produces a carbonate based ore.

(n) New Mexico. Most ore production has been from two large copper mines which produce molybdenum as a byproduct. Ore composition data could not be found for several small districts. However, these cumulatively accounted for only 2 percent of the waste generation.

(o) New York. All production has been from two zinc mines that produce a pyritic ore.

(p) North Carolina. A majority of ore production has been from one mine producing a pyritic copper ore. Data on other ores are unavailable; however, these account for only 33 percent of the state's waste generation, which is relatively small on a national scale.

(q) Oklahoma. All ore production has been from lead-zinc mines in two counties that produce a carbonate based ore.

(r) Oregon. Most ore production has been from a single copper mine producing a pyritic ore. Ore composition data could not be found for a few small districts that produce about 22 percent of the state's wastes.

(s) Pennsylvania. All ore production is from two districts, where ore compositions are known.

(t) South Carolina. The only ore production has been from one gold mine that generated a small amount of waste in the 1930s by mining a pyritic ore.

(u) South Dakota. Almost all ore production has been from one large gold mine producing an ore that contains pyrite with negligible carbonate levels.

(v) Tennessee. Most ore production has been from two districts, one producing a carbonate based zinc ore and the other mining a highly pyritic copper-zinc ore. In the latter case, the pyrite is recovered as a product and converted to iron oxide and sulfuric acid for sale. Ore composition data are missing for a few minor districts, which account for less than 1 percent of the waste generation.

(w) Texas. All ore production is from a pyritic ore body from which mercury and silver have been recovered.

(x) Utah. Most ore production has been for three major districts including the Bingham Canyon Copper District. This district has a two-zoned ore body, with the upper layer being carbonate rich and the lower level containing significant to high levels of pyrite. Data on ore compositions could not be found for a few minor districts that account for less than 1 percent of the wastes generated.

(y) Vermont. All ore production has been from mines which produce a pyritic copper-zinc ore.

(z) Virginia. Most ore production has been from one zinc district where a highly nonhomogeneous ore is produced. The upper layers of the ore body are carbonate rich, the lower levels are sulfide rich. Data on ore compositions could not be found for a few minor districts that account for about 5 percent of the waste generated.

(aa) Washington. Ore composition data could not be found for the old Lake Chelan copper-zinc district. However, composition data are available for about 68 percent of the ores produced in this state.

(bb) Wisconsin. All ore production has been from one zinc ore body that is carbonate based.

USEPA (1985a) estimates the amount of tailings with high acid formation potential produced annually by the copper mining industry. This estimate is based on criteria similar to those described above, with the exception that only those tailings with sulfide content and entirely lacking in carbonate content were classified as having high acid formation potential. It is estimated by USEPA (1985a) that 95 million metric tons of tailings with high acid generation potential are produced annually by this mining segment.

Additional data on pyritic ore bodies are available from several sources and serve as a comparison to and confirmation of the assessment of tailings acid generation potential presented in Table 3-3. The sources of these data are: Martin and Mills (1976) and PEI (1984), which provide descriptions of surface water acidification due to acid releases from mine adits and tailings; TRC (1985), which summarizes and provides commentary on a compilation of environmental degradation incidents associated with the disposal of mining wastes prepared by SCS (1985); and

PEI (1983) and ERCO (1984), which provide analytical data for various mine waste materials at selected mines. Where these data indicated acid releases could be related to a specific ore body, originated from tailings or ore material, and were not (in the case of the TRC/SCS data) challenged as incorrect by any parties, they were tabulated in Table 3-5. The ore bodies to which the information is related, and the acid-generation potential ratings assigned to these ore bodies (from Table 3-3) are also tabulated in Table 3-5.

There is good correspondence between the assessment of high and intermediate acid generation potential made in the present study and the observation of acidic conditions reported by the sources listed. In a few cases, acid formation has been observed for ores ranked as intermediate in acid formation potential. In most of these cases, the ore body involved is highly nonhomogeneous; these cases illustrate that wastes from such ores will generate acids under the right conditions.

For some sites with high acid formation potential, no damage cases have been observed. This lack of damage incidents may reflect site topography, waste disposal practices, or simply lack of survey data. In cases where carbonate rich mine development wastes or tailings are codisposed with spent pyritic tailings, carbonate values present may serve to neutralize any acids formed by pyrite oxidation, thereby preventing acid formation. This may be the case at Leadville, Colorado, where the ore contains sulfides, but the ore body also contains carbonates and is in contact with other carbonate rich formations (Ridge 1970). Drainage observed at Leadville contains some heavy metals but is slightly alkaline in nature (PEI 1983).

The information in Table 3-5 also illustrates the effect of milling on the composition of tailings. A case in point is the tailings pH data presented for the Cripple Creek, Colorado, ore body. Although the mineralization of this ore suggests that tailings from ore milling would exhibit intermediate acid generation potential, the pH data for tailings pond liquids from two gold mines working this ore body indicate alkaline tailings (PEI 1983). This can probably be attributed to the alkaline-based cyanide leaching process employed for gold extraction.

Table 3-5. Data Indicating Acid Generation by Ore or Tailings, Compared to Assessed Acid Generation Potentials for Associated Ore Bodies

| Major ore body | State | Acid generation potential[a] | Acid release cases[b] |  | Empirical data[c] |
|---|---|---|---|---|---|
|  |  |  | Number of sites | Comments |  |
| Central Arizona Copper Belt | AZ | Intermediate | 7 | One site has acid drainage (pH 3.0); acid drainage from tailings reported at additional sites. | Tailings pond liquid at one site had pH of 7.2. Mine drainage at 2 sites had pH of 7.9 to 8.9 (PEI 1983). |
| Mojave | AZ | High | 1 | Acid runoff at one site reported by TRS (1985). | - |
| Mother Lode | CA | High | 10 | Six sites have acid drainage from mine and tailings with pH values from 1.6 to 4.5; others reported by Martin and Mills (1976) have acid drainage from adits. | - |
| Shasta Tinity | CA | High | 4 | Acid mine water reported by Martin and Mills (1976), no pH specified. | - |
| Gilman | CO | High | 2 | Acid tailings drainages (pH 5.1 to 6.3) reported by Martin and Mills (1976). | - |
| San Juan | CO | Intermediate | 3 | Acid drainages from tailings, (pH 6.3 at one site; Martin and Mills 1976.) | One mine had pumpout water of pH 4.8 (ERCO 1984.) |
| Climax | CO | High | 1 | Mine water pH 2.97, acid runoff from tailings, (no pH data) reported by Martin and Mills (1976). | Tailings liquors pH = 7.28 (PEI 1983). |

Table 3-5. (Continued)

| Major ore body | State | Acid generation potential[a] | Acid release cases[b] Number of sites | Acid release cases[b] Comments | Empirical data[c] |
|---|---|---|---|---|---|
| Cripple Creek | CO | Intermediate | 2 | Acidic mine water and tailings runoff (Martin and Mills 1976). | Two samples of gold mine tailings pond liquors in 9.1 to 9.3 pH range (PEI 1983). |
| Coeur d'Alene | ID | Intermediate | 2 | One mine has acid discharge (pH 4, PEI 1984), other has acid discharge of mine water with unspecified pH. | One mine pond had pH 5.6 (PEI 1983), two other mines had tailings pond pHs of 7.27 and 4.40 (ERCO 1984). |
| Silver City | ID | Intermediate | 3 | One site has mine release (pH 3) second has mine release (pH 4.5); pH from tailings at third site unavailable. | - |
| White Pine | MI | Low | 6 | - | One copper mine site had tailings pond liquors of pH 8.14 (PEI 1983). |
| S.E. Mo Lead Belt | MO | Low | 0 | - | Mine waters at 1 site had pH of 7.96; tailings pond liquor at one site was 7.57 and at another site was 8.03. All were gold mines (PEI 1983). |
| Butte | MT | Intermediate | 1 | - | Tailings pond liquor had pH of 8.59 at one copper mine (PEI 1983). |
| Mountain City | NV | Unknown | 1 | Mine drainage (pH 6.5). | - |
| Questa | NM | High | 1 | Open pit drainages with pH values as low as 1.0 cited by Ridge (1970). | - |

---

[a] Based on ore composition data; from Table 3-3.

[b] Total sites listed as having acid leachate or runoff in Martin and Mills (1976); PEI (1984); and TRC (1985). Only sites from TRC (1985) not disputed by any authorities or experts were counted.

[c] As reported by ERCO (1984); PEI (1983).

### 3.2.3 Copper Dump Leach Wastes

(1) Waste volumes. Data regarding volumes of ore[*] placed in copper dump leach sites are available from two primary sources. The first, Sheffer and Evans (1968), provides the cumulative tons of ore present in 17 copper dump leach operations as of 1965. The second, various years of the U.S. Bureau of Mines Minerals Yearbook, provides the volume of ore only for those Arizona copper dump leach operations that are among the leading 15 copper producing mines (of all types) in the state. These data are provided for each year beginning with 1967 and continuing through 1983.

A third identified source of data (Schlitt 1982) covers a single dump leach operation not covered by Sheffer and Evans; the Phelps-Dodge Corporation's New Cornelia Mine in Ajo, Arizona. Available data indicate that this site began dump leaching in 1917.

Dump leach ore volume data available from these sources are summarized by dump leach site in Table 3-6. Significant gaps in data available in the reviewed literature include: volumes of ore placed in dumps since 1965 (including current volumes) at sites not among the top 15 copper producers in Arizona (including at least five sites located outside of Arizona); and cumulative volumes of ore in dumps at sites not covered by Schlitt (1982) or Sheffer and Evans (1968). Data for many operations in Arizona are available only for certain years between 1967 and 1983, as several mines were among the top 15 copper producers in Arizona for only a portion of these years. Volume data are not available for any sites for the year 1966. In addition, it is clear that volume data for several dump leach operations were omitted from all three references cited. Operations in Socaton, Missouri, and Pima and Christmas, Arizona, are mentioned in the Minerals Yearbook (various years), but no ore volume data are given.

---

[*] Materials placed in copper leach dumps include waste rock and overburden wastes containing recoverable copper, and ore mined specifically for the purpose of dump leach extraction. These materials are referred to collectively as ore throughout the text and tables in this section.

Table 3-6. Known Tons of Ore in Copper Leach Dumps, Associated pH Data, and Acid Generation Potentials

| | Ore in copper leach dumps ($10^3$ metric/tons) | | | | | | | Leach liquor pH[a] | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dump leach site | 1 Cumulative to 1965[a] | 2 Cumulative 1967-1983[b] | 3 Cumulative to 1983[c] | 4 Added annually (1983)[d] | Ore body | Pyrite content (% $FeS_2$)[e] | Carbonate content (as % $CaCO_3$)[e] | In | Out | pH Data, release cases[f] | Acid generation potential |
| American Smelting and Refining Co., Silver Bell unit, Silver Bell, Ariz. | 27,210 | 25,268 | 52,448 | 454 | CACD[g] | 0.2-8.0 | 0-20 | | | | Intermediate |
| The Anaconda Company, Butte, Mont. | 29,931 | NA | 29,931 | NA | Butte | 1-13 | 0-11 | 1.9 | 2.2-2.3 | Acid runoff from pit reported by PEI (1984) but not documented. | Intermediate |
| Yerrington mine, Weed Heights, Nev. | 27,210 | NA | 27,210 | closed 1977 | Yerrington | Nil | >20 | 1.2-1.3 | 1.9 | Acid runoff reported (PEI 1984; no pH given). | Intermediate |
| Bagdad Copper Corp., Bagdad, Ariz. | 36,280 | 32,138 | 68,418 | NA | Baghdad | <1 | Nil | 1.4-1.6 | 2.1-2.4 | Leach liquor pH 1.95 (ERCO 1984). | Intermediate |
| Duval Corp. | | | | | | | | | | | |
| Esperanza mine, Sahuarita, Ariz. | 17,230 | 57,676 | 74,906 | 67 | CACD | 0.2-8.0 | 0-20 | 2.5 | 2.3-3.3 | Pregnant heap leach liquor pH 1.90 (PEI 1983) | Intermediate |
| Mineral Park, Ariz. | 4,988 | 30,679 | 35,667 | | Mojave | 5.0 | Nil | 3.5 | 1.24 | | High |
| Inspiration Consolidated Copper Co., Inspiration, Ariz. | 27,210 | 111,198 | 138,408 | 20,608 | CACD | 0.2-8.0 | 0-20 | 2.6-3.0 | >2.0 | Leach liquor pH 1.82 (ERCO 1984). | Intermediate |
| Kennecott Copper Corp.; Utah Copper Division, Bingham Canyon, Utah | 3,628,000 | NA | 3,628,000 | NA | Bingham Cyn | Variable up to 75% | High to nil | 2.8-3.0 | 2.5 | Mine water pH 3.22 (PEI 1983) | High |

146

Table 3-6. (Continued)

| | Ore in copper leach dumps ($10^3$ metric/tons) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Dump leach site | 1 Cumulative to 1965[a] | 2 Cumulative 1967-1983[b] | 3 Cumulative to 1983[c] | 4 Added annually (1983)[d] | Ore body | Pyrite content (% $FeS_2$)[e] | Carbonate content (as % $CaCO_3$)[e] | Leach liquor pH[a] In | Out | pH Data, release cases[f] | Acid generation potential |
| Chino Mines Division, Santa Rita, N. Mex. | 385,475 | NA | 385,475 | NA | Santa Rita | 0.3 - 2.0 | 1-3.4 | 3.5 | 2.5 | Acid runoff from dump leach area; pregnant heap leach liquor pH 2.6; spent leach liquor pH 3.19 (PEI 1983). | Intermediate |
| Ray Mines Division, Ray, Ariz. | 169,156 | 359,211 | 528,367 | 7,317 | CACD | 0.2-8.0 | 0-20 | 2.5-3.8 | 2.1-3.0 | | Intermediate |
| Miami Copper Co., Miami, Ariz. | | | | | | | | | | | |
| Castle Dome Unit | 43,536 | | | NA | CACD | 0.2-8.0 | 0-20 | 2.7 | 2.3 | | Intermediate |
| Copper Cities Unit | NA | 230,304[h] | 273,840[h] | NA | CACD | 0.2-8.0 | 0-20 | 2.6 | 2.5 | | Intermediate |
| Miami Unit | NA | | | NA | CACD | 0.2-8.0 | 0-20 | 1.4 | 2.4 | | Intermediate |
| Pinto Valley | NA | | | NA | CACD | 0.2-8.0 | 0-20 | NA | NA | | Intermediate |
| Phelps Dodge Corp., Bisbee, Ariz. | 42,629 | 2,753 | 45,382 | NA | CACD | 0.2-8.0[h] | | | | | |
| Morenci, Ariz. | NA | 236,691 | 236,691 | 11,731 | CACD | 3.5-8.0[i] | 0-20 | 2.8-3.1 | 2.0-2.2 | | Intermediate |
| Ranchers Exploration & Development Corp., Bluebird mine, Miami, Ariz. | 454 | NA | 454 | NA | CACD | 0.2-8.0 | 10-15 | 3.8-4.2 | 2.8-3.2 | Leach liquor pH 3.19 (PEI 1983). | Intermediate |

Table 3-6. (Continued)

| Dump leach site | Ore in copper leach dumps ($10^3$ metric/tons) 1 Cumulative to 1965[a] | 2 Cumulative 1967-1983[b] | 3 Cumulative to 1983[c] | 4 Added annually (1983)[d] | Ore body | Pyrite content (% $FeS_2$)[e] | Carbonate content (as % $CaCO_3$)[e] | Leach liquor pH[a] In | Out | pH Data, release cases[f] | Acid generation potential |
|---|---|---|---|---|---|---|---|---|---|---|---|
| J.H. Trigg Co., Tyrone, N. Mex. | | | | | | | | | | | |
| Property No. 1 | 136 | NA | 136 | NA | Santa Rita | 0.3-2.0 | 1-3.4 | 2.2 | 3.0-3.5 | | Intermediate |
| Property No. 2 | 91 | NA | 91 | NA | Santa Rita | 0.3-2.0 | 1-3.4 | NA | NA | | Intermediate |
| Zontelli Western Mining Co., Page, Ariz. | 454 | NA | 454 | NA | CACD | 0.2-8.0 | 0-20 | NA | NA | | Intermediate |
| Twin Buttes, Ariz. | NA | 18,244 | 18,244 | 18 | CACD | 0.2-8.0 | 0-20 | NA | NA | | Intermediate |
| Metcalf, Ariz. | NA | 45,627 | 45,627 | NA | CACD | 0.2-8.0 | 0-20 | NA | NA | | Intermediate |
| Total | | | 5,589,461 | 40,200 | | | | | | | |

[a] From Sheffer and Evans (1968).

[b] From USBM Minerals Yearbook, Volume II, various years. Ores placed in leach dumps not available for all mines for all years (see text for details regarding data gaps).

[c] Total of Columns 1 and 2. Data unavailable for 1966 for all operations, and for other years for several operations (see text for details regarding data gaps).

[d] From USBM Minerals Yearbook 1985, Volume 2.

[e] From Ridge (1970).

[f] Information compiled from PEI (1983); PEI(1984); ERCO (1984).

[g] Central Arizona Copper District.

[h] Total for all Miami operations (USBM Minerals Yearbook, various years).

[i] Pyrite content available for individual mine (Ridge 1970).

A second factor hindering the assessment of dump leach waste volumes is the definition of those leach dump ores that are waste. A common practice at dump leach sites is to continue piling fresh ore onto an established site, and to continue leaching these sites indefinitely. Old ore which may be exhausted of copper values remains within the active operation at such sites. In addition, sites now closed may not be permanently abandoned; they are likely to resume operations when copper prices make this economically feasible.*

Only an unquantifiable portion of the ore in leach dumps at the active sites listed in Table 3-6 can therefore be considered permanently disposed of. The portion of such ores that may be considered permanently disposed wastes at sites presently closed for operation is equally unquantifiable, and may range from none to all of the leach dump tonnage.

The lack of a definition of waste and the lack of a quantification of leach dump ores which can be defined as wastes represent an important gap in data available in the reviewed literature. It can be safely stated, however, that all leach dump material quantified in Table 3-6 (and placed on leach dump sites in the future) will eventually become waste and that, in the long term, waste generated will equal ore placed on leach dumps.

(2) Acid generation potential. All leach dump material contains acid during the active operation of the site. The pH of leach liquor is usually adjusted to within the range of 1.5 to 3.0 before it is introduced to the top of the dump, in order to ensure sufficient acidity for the dissolution of copper within the dump (Sheffer and Evans 1968).

This added acid can be expected to result in low-pH leachate for some time after dump closure, even from dump sites containing alkaline ores. A case in point is the leach dump consisting of carbonate based ores at Yerrington, Nevada (Table 3-6). Although this operation was closed in 1977, information presented by PEI (1984) indicates a continuing acid runoff problem.

---

*Personal communication with Reese Groves, Supervising Metallurgist, Salt Lake Research Center, U.S. Bureau of Mines.

Ores in leach dumps predominantly containing pyrites are expected to continue generating acid after the closing of the dump operation. The chemical environment maintained during dump leach operation ensures that pyrite oxidation will take place and, given adequate infiltration from rainfall, this oxidation process will continue following the abandonment of the dump. It may be expected, however, that some portion of the original pyritic content of these ores is oxidized and removed during the active life of the operation. Thus, the residual pyritic (and carbonate) content and acid generation potential of abandoned dump leach wastes is not that of the original ore. No data were available in the reviewed literature regarding the extent of change in ore composition during dump leaching.

In Table 3-6, leach dump ores are ranked according to their assessed potential for acid generation following disposal or abandonment. This ranking is based on: ore mineralization, pH change of leach liquor passing through the ore (assuming that infiltrating rainwater will also be moderately acidic and will, therefore, experience a similar change in pH), and site survey data.

Because these survey data indicate that even leach dumps consisting of predominantly carbonate ores continue to release acids for at least several years following shutdown of active operations, it is apparent that all dump leach wastes have some potential for acid generation. Hence, all wastes in Table 3-6 were assigned at least intermediate acid generation potential. Those consisting of highly pyritic ores were ranked as having high acid generation potential.

The data in Table 3-6 indicate that at least 5.6 billion tons of ore are accumulated at dump leach sites at present, and at least 40 million tons are placed on dump leach sites annually (1983 figure). Because of the data gaps outlined, these figures are known to understate actual cumulative and annual amounts of wastes.

## 3.3 Semi-Quantitative Estimate of Total Acidity Contained in Mine Wastes

The following section presents an estimate of the total amount of net acidity contained in mine and beneficiation waste material and dump leach ores accumulated as of 1983 and generated during 1983. This estimate is severely limited by available data, and must be considered semi-quantitative in that numerous sources of error contribute to a wide, although unquantifiable, margin for error in the final values. Some of the more significant of these errors include:

- inability of the estimation method to account for the effects of beneficiation and vat leaching processes, dump leaching, or natural weathering on the amount of pyrite or carbonate remaining in wastes relative to that in the original ore body (estimates are based on ore body mineral content and disregard such factors as the amount of sulfide removed during concentration and shipped with the metal concentrate);
- lack of cumulative quantity or mineralization data for mine development wastes or vat leached tailings (these wastes are disregarded);
- incompleteness of leach dump ore volume and mineralization data;
- wide ranges in pyrite and carbonate contents as reported by Ridge (1970) for most ore bodies (central values in the reported ranges selected for this estimation may not be representative);
- lack of mineralization or quantity data for tailings generated since 1981; and
- lack of mineralization data for a portion of the tailings generated since 1910 (these tailings are disregarded).

The estimation of total acidity is based on acid-base accounting for individual ore bodies which are the sources of mine, beneficiation, and leach dump wastes. It incorporates the assumption that all pyrites in the ore will be present in waste material and will eventually be fully oxidized, resulting in four equivalents of acidity per molecule of $FeS_2$. A further assumption is that all acid consuming minerals (expressed in terms of carbonate, $CaCO_3$) will fully solubilize in

151

interstitial waters, resulting in an acid neutralizing capacity of two equivalents per molecule. All acidic and acid neutralizing minerals are assumed to be equally available for neutralization reactions and the ultimate potential acidity is assumed to be only that which is present in excess of the total acid neutralization capacity of the ore (Sobek et. al. 1978).

As illustrated previously (Section 3.1), the stoichiometric equation for pyrite oxidation and the atomic weights of the associated elements indicate that one percent of pyrite in ore will oxidize to produce 1.67 percent acidity, expressed as $CaCO_3$ equivalents. Carbonate content in ore is expressed as percent $CaCO_3$. Therefore, the acid-base accounting equation is:

$$1.67\ (\%\ FeS_2) - \%\ \text{carbonate} = \text{potential acidity}$$

where

potential acidity is expressed in terms of percent $CaCO_3$ equivalents.

As stated earlier, the percent pyrite and percent carbonate values used in cases where available data indicate concentration ranges is the central value in each range. Mineralization is expressed as a range because of the nonhomogeneity of ore mineral content. This selection of a central value assumes that the central value approximates the mean concentration throughout the ore body, and that ore placed in leach dumps or tailings is disposed of in equal amounts from all sections of the ore body and is well mixed. At some sites, especially mining sites in which oxidized ore zones overlie pyritic zones such as numerous mine sites within the Central Arizona Copper belt (Ridge 1970) and the Berkley Pit mine operated at Butte, Montana,* this is not the case. Oxidized ore was mined at some sites for extended periods, until the pyritic layer of the ore body was reached, at which time mining of predominantly pyritic ores began.* For this reason, ores from ore bodies for which the

---

*Personal communication with Reese Groves, Supervising Metallurgist, Salt Lake Research Center, U.S. Bureau of Mines.

152

ly available quantitative mineralization data were expressed in terms of very wide ranges relative to the central figure were not included in this estimate.

Based on available qualitative and quantitative information, of the total tons of copper, gold, lead, silver, and zinc ore milled in the U.S. between 1901 and 1981, approximately 64 percent, or 5.3 billion tons, were assessed to have intermediate or high acid generation potential (Section 3.2 and Table 3-3). Quantitative ore mineralization data that allow an acid-base accounting estimate are available for approximately 17.5 percent of this 5.3 billion tons, or approximately 930 million tons of ore milled by these mining segments over the stated time period. The results of the total potential acidity estimate for this portion of the ore milled is presented in Table 3-7.

In addition to the volume of ore milled, quantitative ore mineralization data are available for ore bodies from which approximately 66 million tons of ore have been placed in copper dump leach operations. This figure represents approximately 1.2 percent of all known ore in copper leach dumps as of 1983. The ores used in this estimate are therefore a small portion of those total ores mined and beneficiated that are likely to generate acid; they also cannot be demonstrated to be representative of the associated industry segments. The figure for total potential acidity (104 million tons as $CaCO_3$ equivalents) presented in Table 3-7, then, represents only a very small, undefinable portion of the total potential acidity contained in mining wastes nationwide.

The common definition of potentially toxic material based on acid-base account results is: any rock or earth material having a net potential calcium carbonate deficiency (or net potential acidity) of 5 tons of calcium carbonate equivalency per 1,000 tons of material, or 0.5 percent as $CaCO_3$ equivalents (Sobek et al. 1978). This definition, when compared with the net potential acidity values in Table 3-7, provides an additional indication of the amount of mining and beneficiation wastes that represent a potential acidity hazard.

Table 3-7. Total Potential Acidity of Wastes (Where Quantifiable)

| Ore body | State | Counties | Ore pyrite content (as % Fe$^{S}$ $_{2}$)** | Ore pyrite content (as % CaCo$_3$ equivalents) | Ore carbonate content (as % CaCo$_3$)** | Potential net acidity (as % CACO$_3$ equivalents) | Ore processed (1910-1981) (thousands of metric tons)** | Known ore placed in leach dumps (thousand of metric tons)** | Total potential acidity (thousands of tons of CACO$_3$ equivalent) |
|---|---|---|---|---|---|---|---|---|---|
| Mineral PK | AZ | Mojave | 5.0 | 8.0 | Nil | 8.0 | 95,000 | 35,667 | 10,453 |
| Mother Lode | CA | Mariposa, Tuolumne, Calavaras, Amador, El Dorado, Placer, Nevada, Sierra, Yuba | 1 to 4<br>(2.0)* | 3.2* | Nil | 3.2 | 38,000 | | 1,216 |
| Shasta-Trinity | CA | Shasta, Trinity | 10* | 16* | Nil | 16 | 3,500 | | 560 |
| Gilman | CO | Eagle, Gilpin | 30 | 48 | Nil | 48 | 10,600 | | 5,088 |
| Climax | CO | Summit | 2 to 3<br>(2.5)* | 4.0* | Nil | 4.0 | 1,300 | | 52 |
| Coeur d'Alene | ID | Shoshone | 1 to 3<br>(2)* | 3.2* | 1.0* | 2.2 | 109,000 | | 2,398 |
| Silver City | ID | Owyhee | 1.0 | 1.6 | Nil | 1.6 | 3,300 | | 53 |
| Butte | MT | Silver Bow | 0 to 13<br>(6.5)* | 10.4 | 0 to 11<br>(5.5)* | 4.9 | 474,000 | 29,931 | 24,692 |
| Questa | NM | Taos | 2.0 | 3.2 | Nil | 3.2 | 3,000 | | 96 |

154

Table 3-7. (Continued)

| Ore body | State | Counties | Ore pyrite content (as % Fe$^{S}$ $_{2}$)** | Ore pyrite content (as % CaCo$_3$ equivalents) | Ore carbonate content (as % CaCo$_3$)** | Potential net acidity (as % CACO$_3$ equivalents) | Ore processed (1910-1981) (thousands of metric tons)** | Known ore placed in leach dumps (thousand of metric tons)** | Total potential acidity (thousands of tons of CACO$_3$ equivalent) |
|---|---|---|---|---|---|---|---|---|---|
| Balmat | NY | St. Lawrence | 18.5 | 29.6 | 6.5 | 23 | 28,000 | | 6,440 |
| Ashe | NC | Ashe | 25-60<br>(40)* | 64 | Nil | 64 | 1,300 | | 832 |
| Baker | OR | Baker | 4 | 6.4 | Nil | 6.4 | 1500 | | 96 |
| Homestake | SD | Lawrence | 7.5 | 12.0 | Nil | 12 | 97,000 | | 11,640 |
| Copperhill | TN | Polk | 50 | 80 | 10* | 70 | 57,000 | | 39,900 |
| VanStone | WA | Stevens | 10 | 16 | Nil | 16 | 5,200 | | 832 |
| TOTALS: | | | | | | | 928,000 | 66,000 | 104,000 |

*Central value of known mineralization range.

**Data adapted from Tables 3-3 and 3-6.

Potential acidity content does not indicate acid generation or release rates. Ores with high net potential acidity may not presently be releasing acid to the environment and, conversely, those with low acidity may presently be causing environmental degradation. Factors determining acid generation and release rates are detailed in Section 3.5; the acid-base balance is shown therein to be a poor indicator of these rates.

## 3.4 Assessment of Future Waste Generation Rates

The determining factor for the rate of mining activity and mine/beneficiation/leach dump waste generation is the available price for the produced commodity. Commodity prices are affected by a complex array of political, economic, and technical factors which include: economic activity of domestic ore, concentrate or precipitate consuming industries (in turn affected by prices available to these consumers for their products); the global demand for mining/beneficiation products; current stockpiles of these products; competition from the mining industries of other countries (often affected significantly by the strength of the dollar versus foreign currencies); the relative attractiveness of investments other than mining commodities (often causing dramatic fluctuation in commodity prices as investors change investment positions); legislation and government programs which affect import tariffs or rates, affect the manner of operation and economy of mine/beneficiation operations, or affect government purchasing of mine commodities; advances in mining/beneficiation/dump leach technologies which allow more economical production of mine commodities; and the grade of ore reserves available to individual mine operations.

A discussion regarding the recent past and current trends in these factors for the copper, lead, and zinc mining industries follows. A similar discussion for the gold and silver industries was presented previously (Section 2).

### 3.4.1 Copper

The average copper price for 1984 was the lowest in real terms since World War II price controls (Jolly and Edelstein 1984). Major factors contributing to declining prices include (Jolly and Edelstein 1984):

- Large world stocks of refined copper. These stocks declined during 1984 but remain high enough to contribute significantly to copper price depression.
- Continued increases in production rates of other countries and the strength of the dollar versus other currencies, which rendered U.S. products generally unable to compete on world markets.
- High imports of copper and copper products, which offset the general growth of copper consuming industries (especially those tied to the strong housing, automotive, and electronics industries) in terms of markets for domestic copper production.
- Rejection by the Administration of a copper industry petition (under Section 20 of the Trade Act of 1974) to impose tariffs and quotas on copper imports.
- A prediction of high U.S. interest rates in the second quarter of 1984 that caused a rush of investors away from copper commodities markets into other investments and a consequent sharp decline in copper prices.

These factors combined to bring about a decline in the U.S. copper industry, and in copper mining activities. Many mining and beneficiation facilities remained closed or operated at a fraction of capacity (Jolly 1985).

The factors listed above (except the last one) can be expected to continue depressing copper prices in the near future. An additional factor that may affect prices is the final form of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) reauthorization legislation (probably to be enacted in early 1986) and the tax, if any, imposed on copper by that legislation (Jolly and Edelstein 1984).

Jolly (1985) presents a forecast of the end-use demand for copper for the year 2000. This forecast is based on historical correlations of end-use demand with several economic factors including the GNP, population, private domestic investment rates, construction activity, and others. Expected contingencies, such as technological advances and foreign competition, are also factored in. The forecast is for a 39 percent increase in annual end-use copper demand for the year 2000 over the 1983 demand level, or a demand for 2.8 million tons of copper in the year 2000. Of this amount, 2.1 million tons represents demand for primary copper (i.e., mine production). This figure is based on an average 1.7 percent annual expected increase in demand for primary copper for the years 1984 to 2000.

Based on historical trends in the portion of domestic demand supplied by domestic mines, Jolly (1985) estimates that annual U.S. primary production of copper will exceed 1983 figures by approximately 6 percent in 1990, and by approximately 35 percent by the year 2000. These figures provide a basis for estimating future waste generation rates associated with this industry segment; growth in waste generation may be expected to equal that in primary production. The portion of these wastes exhibiting acid generation potential cannot be established, but can be estimated by reference to the portion of all wastes with high or intermediate acid generation potential presented in Table 3-3.

Using Jolly's (1985) figures for primary production in 1990 (1.1 million metric tons) and the ratio of ore (including flotation and vat leaching) milled to primary production from 1982 through 1984 (Jolly and Edelstein 1984) of approximately 163 to 1, it can be estimated that 180 million tons of copper ore will be milled in 1990. This approximates the tons of tailings that will be generated. The 1978 through 1983 ratio of mine development waste to ore (from Table 3-2) is approximately 1.8; it can be estimated that 323 million tons of mine development waste will be generated in 1990 on this basis. The tons of ore that will be placed in leach dumps cannot be estimated with available data.

Similar calculations for the year 2000 result in a projected 228 million tons of copper ore milled (and a similar tonnage of tailings generated) in that year. Approximately 411 million metric tons of mine development waste will be generated.

Using 1984 annual rates through 1989, 1990 rates through 1999, and the above figures for the year 2000, the projected cumulative copper ore mined and milled (and approximate tailings generated) for the period 1984 through 2000 is 2.7 billion tons. Estimated mine development wastes will be 4.9 billion tons for the period.

Coppa (1984) makes a projection of the volume of tailings to be generated by the copper milling industry in the U.S. based on 1981 production figures and ore reserves. Because 1981 production was high (nearly 50 percent greater than that for 1983; Jolly 1985) the projections by Coppa may also be high. Coppa projects that 4.5 billion* metric tons of tailings will be generated by copper milling operations from 1982 through 2001. Note that this figure includes tailings from the processing of all copper ores, both pyritic and non-pyritic.

### 3.4.2 Lead

Lead prices fluctuated considerably during 1984. The average U.S. producer's price for the year was up slightly since 1983, reaching the 1982 price level. However, prices at year end were lower than those for January. Influencing factors included (Woodbury 1984):

- Disruption in both domestic and foreign mine output due to lengthy strikes here and abroad, and floods, producer-purchaser disputes, landslides, and guerilla activity abroad.
- Increase in domestic lead consumption in virtually every end use except gasoline additives, radiation shielding, and lead based solder. Battery manufacture, the largest single end-use of lead, increased nearly six percent based on new battery shipments for the year, reaching the highest level since 1979.

---

*As revised by Luis Coppa, personal communication, December 12, 1985.

15

- A moderate increase in net imports of all lead products for the year resulting from lower prices on the world market than those available in the U.S.

Mainly because of seven- and eight-month strikes that affected large mines in Missouri, lead production in 1984 was the lowest since 1967. This low production follows a steady decline of net mine production for the previous three years. This decline is attributed to a general world wide recession and low world wide demand for lead (Woodbury 1984).

Factors expected to influence lead prices in the near future include: development of new technologies requiring lead, including lead battery powered tractor motors, lead-in-asphalt pavement, and lead wrapped cable; the phasing out of lead based gasoline; and the taxation (if any) imposed on lead by CERCLA reauthorization legislation (Woodbury 1984).

Woodbury (1985) analyzed past production trends, domestic demand-to-production ratios, and expected general economic trends as they affect the lead mining industry and, based on these, presents a projection of mine production of recoverable lead through the year 2000. Production rates for the years 1990 and 2000 are expected to exceed the 1983 production rate by 15.8 percent and 38.1 percent, respectively. The associated production volume figures are 520 thousand metric tons of lead in 1990, and 620 thousand metric tons of lead in 2000. Using the ratio of lead ore mined in 1983 (Willard 1984) to lead produced in 1983 (Woodbury 1983) of 18.7 to 1, it can be estimated that roughly 9.7 million metric tons of crude lead ore will be mined in 1990, and 11.6 million metric tons will be mined in 2000.

The portion of this ore that will be concentrated in mills as opposed to that portion going directly to smelters cannot be determined. Hence, mill tailing estimates cannot be made with these data. Using the 1983 ratio of mine development wastes (Willard 1984) to lead produced (Woodbury 1983) of 5.1 to 1, it can be projected that 2.6 million metric tons of mine development waste will be generated in 1990, and 3.2 million metric tons will be generated in 2000. If 1983 annual figures for mine development waste are used for 1984 through 1989, the 1990 generation rate is used for 1990 through 1999, and the projected generation rate for the year 2000 is used for that year, an estimated cumulative amount of mine development waste generated by the lead mining industry for that period of 1984 through 2000 can be projected. This projected figure is 40.2 million metric tons. Note that not all of these wastes will have acid generation potential, however.

Using 1981 generation figures and known ore reserves, Coppa (1984) estimates that 269 million metric tons of mill tailings (from both pyritic and non-pyritic ores) will be generated by the combined lead-zinc mining industries in the period 1982 through 2001.

### 3.4.3 Zinc

The most recent mine production data for zinc, that for 1983, indicate that mine production of this commodity continued on a decline that began in 1981. Zinc production for 1983 was the second lowest (after 1979) since 1950. However, average annual zinc prices increased slightly for the year as compared to 1982 (Jolly 1983). Factors affecting price and mine production included (Jolly 1983):

- Large purchases and announced plans for additional purchases of domestic zinc by the U.S. Mint.
- Increases in zinc end-use consumption for most categories, especially those tied to housing and automotive industries.
- The third highest imports of slab zinc in history, which more than offset significant increases in U.S. zinc end-use consumption.

Factors likely to affect mine production of zinc in the near future include the modernization of a number of electrolytic zinc plants and zinc smelters, which will increase their cost competitiveness with foreign zinc producers and, therefore, demand for zinc mine products (Jolly 1983).

Based on recent economic trends and domestic zinc production versus consumption trends, Jolly (1985b) projects that U.S. mine production of zinc will increase over 1983 figures by 63 percent (to 450 thousand metric tons) in 1990, and by 155 percent (to 700 thousand metric tons) in the year 2000.

The ratio of zinc crude ore mined (Willard 1984) to metal produced (Jolly (1985b) for 1983 is 20.7 to 1. Mine development waste (Willard 1984) to metal produced for 1983 is in a ratio of 2.1 to 1. These ratios form the basis for the following projections: in 1990, 9.0 million metric tons of zinc crude ore will be mined, and 0.95 million metric tons of mine development waste will be generated; in 2000 these values will be 14.5 million metric tons of ore and 1.5 million metric tons of mine development waste. Note that a portion of the ore produced (unquantifiable with available data) will go directly to smelters, and will not form tailings. A portion of the tailings generated will also be from non-pyritic ore and will, therefore, have little or no acid formation potential.

Cumulative mine development wastes projected for the zinc mining industry for 1984 through 2000 (using 1983 data for 1984 through 1989, 1990 data for 1990 through 1999, and 2000 data for the year 2000) equal 12.9 million metric tons. These include both pyritic and non-pyritic wastes

## 3.5 Methods for Assessing Acid Generation and Release Rates

Factors contributing to the rate of acid release from mining wastes are numerous, complex, and site-specific. Their great variability from site to site, among formations within individual ore bodies, and over time make acid release difficult to model reliably, even on a site-specific basis. Reliable generalized models, applicable to nation wide wastes and based on limited input parameters are not feasible (Martin and Mills 1976).

In assessing the rates of acid release from mine wastes, two processes must be considered: (1) the rate of acid formation and (2) the rate of removal of acid from the waste. The significant parameters determining the rates of each process are described in the following subsections.

### 3.5.1 Acid Formation

The oxidation of base metal sulfides to form sulfuric acid proceeds at a highly variable rate and depends on the following factors:

1. Pyrite morphology. Carrucio (n.d.), and Smith and Schumate (1970 as reviewed by Burt 1981) have concluded that the most important factor determining the rate of pyrite oxidation is the surface area of pyrite particles available for reaction. All other factors being equal, systems containing pyrite in fine particulate form, or in a form with convoluted or pitted surfaces (such as frambodial or mossy pyrites) generate acid at greater rates than systems containing massive pyrite deposits.

2. Presence of carbonates. As discussed previously, carbonate (largely present as a $CaCO_3$ or limestone, and to a lesser degree as other carbonate minerals) has the capacity to neutralize sulfuric acid formed by the oxidation of pyrite. Perhaps more importantly, when soils containing carbonates preceed pyritic wastes in the water infiltration route through a system, water reaching the pyritic material can be of high enough pH to prevent the initiation of pyrite oxidation (Carrucio n.d.). Thus, the relative location of carbonates to pyrites with respect to water flow can cause carbonate materials to exert a preventive effect on acid generation rates greater than the neutralization effect predicted by acid-base accounting. This preventive effect may exist for a finite period of time, however, until all carbonate material is dissolved out of the system. Once this occurs, generation of acid may begin.

3. Availability of water. Oxidation of pyrite in mine waste materials requires the presence of water (Morth 1972). Water serves as a solution medium for reaction products and transports these products away from the surface of pyrite deposits.

4. Presence and activity of iron oxidizing bacteria. Where ferric ion is present in solution at a reactive site, this ion can contribute significantly to the rate of pyrite oxidation by serving as an oxidizing agent. (Smith and Shumate 1970, as reviewed by Burt 1981). The rate limiting step in this oxidation route, however, is the oxidation of ferrous iron to ferric iron, an especially slow reaction in a low pH environment. The bacteria, *Thiobacillus ferrooxidans*, has the capacity to greatly increase the rate of oxidation of ferrous to ferric ion, thereby increasing the presence of the latter ion in solution and indirectly catalyzing pyrite oxidation (Burt 1981; Geidel 1979; Morth 1972). Morth (1972) reviews several studies demonstrating 10- to 50-fold increases in the rate of pyrite oxidation following the addition of *T.ferrooxidans* to a system, and increases in the ferric to ferrous iron ratios in systems following introduction of this species. *T.ferrooxidans* can survive only in environments with pH levels of 6.2 or lower,* one of the reasons that alkaline waters entering pyritic mine wastes can inhibit pyrite oxidation.

5. Relative formation kinetics and flushing intervals. The dissolution of calcium carbonate in water is rapid, and an equilibrium concentration of alkalinity in interstitial waters (approximately 700 mg/l as $CaCO_3$ at a maximum; Geidel 1979) is reached in a short time following water introduction to the system. The concentration of pyrite oxidation products in interstitial waters, on the other hand, is rarely limited by the solubility of these reaction products. This concentration is instead limited by the rate of the pyrite oxidation reaction (Geidel 1979). The maximum equilibrium solubility of these products is several orders of magnitude greater than that of carbonate (Geidel 1979), allowing the oxidation of pyrites and the gradual build-up of acidity to continue unhindered over extended periods of time. The implications of these differing kinetics of formation are two fold: in systems where

---

*Personal communication with Frank Caruccio, December 16, 1985.

carbonate and pyritic materials are segregated, the intervals between flushing of interstitial waters will regulate the degree of acidity in the leachate produced. Where flushing intervals are short, leachate is alkaline. Long intervals between flushing permits the buildup of high concentrations of acid in interstitial waters adjacent to pyrites, until acid concentrations greatly exceed the neutralization capacity represented by the maximum equilibrium concentration of carbonates. Leachate following a long flushing interval in such systems is therefore acidic. Hence, the frequency of rainfall and water infiltration to wastes can be a significant determining factor in acid release (Carrucio and Geidel 1981).

The second implication of the differing formation kinetics of carbonates and acids is important in climates with frequent rainfall, or in systems with a constant flow through of water. The rapid dissolution of carbonates into waters flowing through a frequently flushed system results in their selective removal, resulting in the loss of the acid neutralizing capacity of the system. This can result in the eventual generation of greater acidity than predicted through acid-base accounting, (Carrucio n.d.).

6. Availability of oxygen. Morth (1972) reviews several studies that indicate a direct relationship between oxygen concentration in the liquid or vapor phase of a pyritic system and pyrite oxidation rates. He concludes that over normal atmospheric conditions, the relationship can be taken as a linear (first-order) dependency. Oxygen is the predominant oxidant of pyrite in most abiotic systems, and serves as the ultimate electron acceptor (and must therefore be readily available) in *T. ferrooxidans* catalyzed systems (Lou et al., as reviewed by Morth 1972).

7. Temperature. Morth (1972) and Paciorek et al. (1980, as reviewed by Burt 1981) found that pyrite oxidation rates are directly related to system temperature, and approximately double with a temperature increase of 10 °C.

Carrucio (1985) presents preliminary results of a comparative study of the available techniques for predicting the rates of acid generation from mine materials. This researcher categorizes the available techniques into two groups, static and dynamic. The former group consists of techniques for analysis of mine whole-rock material for sulfur content and acid neutralization potential. The principle of acid-base accounting is then applied to the resulting data. As previously discussed, these techniques cannot account for kinetics of acid and base formation, and provide only a rough indication of total potential acid formation and potential acid leachate problems.

The second group of techniques (dynamic tests) consists of various simulated weathering and controlled leaching techniques in which samples of mine materials are placed in containers or columns of various descriptions and leached with water to simulate field leaching conditions. Although expensive and time consuming, these tests appear to best simulate the rate of acid release under field conditions. Carrucio (1985) concludes from preliminary results (based on comparisons of cumulative acid generated and rate of generation over 80 days under test and field conditions) that the column weathering technique, utilizing a relatively large sample size (2-3 kg) and periodic water introduction simulating rainfall intervals (7-day intervals between introduction), produces acid generation rates most closely reflecting those of mine waste material under field conditions (Carrucio 1985).

While this investigation is ongoing at this writing, it appears from the above result that site-specific simulated weathering test results constitute a valuable input for the modeling of acid releases from mine waste materials.

A potential alternative to the development of simulated weathering test data is the application of an acid mine drainage model developed by Jaynes et al. (1984a). This model describes the oxidation of pyrite in a reclaimed coal strip mine environment, but is applicable with modification to unsaturated mine waste disposal sites.* The model accounts for direct oxygen and ferric iron oxidation of pyrite, and for the activity of T.ferrooxidans. It assumes that diffusion is the main mechanism of oxygen transport within mine waste material, an assumption which is appropriate unless very large diameter rock waste material is to be modeled (in which case convective transport predominates; Jaynes et al. 1984a). The model has been shown to provide estimated leachate concentrations within the ranges measured at one reclaimed coal strip mine site (Jaynes et al. 1984b).

Waste specific data required for the use of this model include: pyrite content; fraction of coarse fragments; leaching rate; temperature; fragment thickness; diffusion coefficient, first-order reaction coefficients for the direct oxygen and ferric iron oxidation of pyrite; air-filled porosity, tortuosity, presence, or absence of T.ferrooxidans; and acid consumption and netrualization characteristics. The model is therefore data intensive. It has yet to be verified for metals mining wastes.

### 3.5.2 Removal Mechanisms

The mechanisms affecting removal of acids formed within pyritic mine waste systems are a function of the method of waste disposal. For mine development wastes and waste leach dump ores, final waste disposal is in the form of piles, while tailings and waste solutions are disposed of in ponds or impoundments. The mechanisms of acid removal from waste in these two types of disposal site and factors determining the rate of removal are outlined below.

(1) Waste piles. Mechanisms of acid transport from waste piles include: seepage of acid bearing water through liners or soil layers beneath piles to the underlying vadose zone and ground water; seepage of

---

*Personal communication with Frank Carrucio, December 16, 1985.

acid bearing waters from the lower external surfaces of piles to the surrounding ground surfaces or water flow channels, ultimately resulting in acid introduction to surface waters; and runoff of water bearing dissolved acids from the surface of the waste piles, also ultimately resulting in introduction of acids to surface waters.

That portion of precipitation from each storm event which infiltrates into a waste pile (and eventually contributes to seepage) is determined by the sorptivity and saturated hydraulic conductivity of the waste material, and the rate and duration of rainfall (Harries and Ritchie 1983). The runoff fraction is the difference between total precipitation and the infiltration. Annual infiltration can be determined by summation of the infiltration fraction of individual rainfall events.

Because many waste piles and leach dumps associated with mining consist of large rock material (ranging from several inches to several feet in average diameter for leach dumps; Sheffer and Evans 1968), the sorptivity of this material is generally great, and the infiltration fraction of precipitation is much greater than the runoff fraction. In studying the runoff regime for a mine waste rock dump, Harries and Ritchie (1983) concluded that infiltration accounted for 85 percent of rainfall, and that water infiltrating through the dump was of far greater significance than runoff in determining pollutant release from wastes of this nature. A second finding of these researchers is that the prediction of runoff and infiltration rates is most reliable when the nonhomogeneity of mine wastes are taken into account. As discussed previously, mine waste piles and leach dumps are commonly highly nonhomogeneous with respect to both physical and chemical properties. Harries and Ritchie (1983) found that the best modeling results were obtained through testing the characteristics of many points at the pile surface, estimating the surface area represented by each test location, and using a weighted average for hydrologic parameters.

170

Total annual recharge of water to a waste pile is the difference between annual infiltration and evapotranspiration (Enfield et al. 1982); and the total volume of water entering a waste pile is the product of recharge and surface area. The velocity of water movement through the portion of a waste pile which is unsaturated (i.e., not affected by water mounding at the bottom of the pile) is a function of the recharge rate and the initial volumetric water content of the waste material (Enfield et al. 1982). The total flux of water reaching the bottom of the waste pile is equal to the difference between recharge volume and storage of water within the pile. Storage is a function of the difference between initial moisture content (at the start of a rainfall event or series) and the field capacity of waste material (i.e., the water content above which downward flow of water due to gravity begins). The evapotranspiration and storage terms can be significant for waste piles located in arid climates, reducing the volume of water reaching the bottom of the pile.

In as much as the mode and rate of acid bearing water release from a pile (and hence the degree of impact on receiving streams or aquifers) is more closely associated with the rate of water flux downward through the pile than with the total flux volume, methods of estimating flux rate are important to acid release analysis. Such a method is presented by Hillel (1980); the rate of downward flux is shown to be related to: degree of soil saturation resulting from a storm event (a function of infiltration and initial soil moisture); and the relationship between soil hydraulic conductivity and soil moisture (a function of soil conductance and diffusivity). This method is applicable to the estimation of water flux through fine, unsaturated materials. Jaynes et al. (1984a) state that Darcy type flow modeling (as assumed by Hillel's method) is not an appropriate assumption for coarse materials. however, when acid bearing water reaches the bottom of a waste pile, there are two routes by which it may be released to the environment, seepage through liner material or soil beneath the pile, and seepage through the side walls at the foot of the pile.

Factors determining the relative importance of these rates include: rate of water flux to the bottom of the pile; permeability of the material underlying the waste pile (or leach dump); permeability (i.e., horizontal hydraulic conductivity) of the material constituting the lowest several feet of the waste pile; and the slope of the underlying topography. Where a liner or soil of low permeability underlies a waste pile (often the case in dump leach operations; Sheffer and Evans 1978) the rate of water flow through this underlying liner is often less than that of water reaching the bottom of the heap. This results in the formation of a mound shaped saturated zone within the pile, and the seepage of water through the side walls at the foot of the pile. Where this mounding effect occurs, an important parameter in the estimation of seepage both through the underlying soil and from the foot of the waste pile is the height of the top of the water mounding above the bottom of the liner, and above the point of water seepage from the foot of the pile.

In at least one case cited by Sheffer and Evans (1968), an impermeable synthetic liner was installed on the site of a dump leach operation before construction of the dump. In cases where such liners have been installed, the rate of acid bearing water transport to underlying soils and ground water is related to the likelihood and degree of liner failure. A stochastic approach to the estimation of liner failure has been advanced by USEPA (1985). This approach is discussed in further detail in the following subsection covering tailings impoundments.

As the foregoing discussion illustrates, the estimation of moisture flow through a waste pile and leach dump, an important portion of any estimate of the rate of acid release from the waste site, is highly site-specific and is data intensive. Table 3-8 presents a summary of the minimum site data required for the estimation of water movement.

Table 3-8. Minimal Data Requirements for Estimation of Water Flux Through and Seepage From Waste Piles

| |
|---|
| Sorptivity |
| Saturated hydraulic conductivity |
| Rainfall patterns (frequency, duration, intensity, total annual precipitation) |
| Saturated and unsaturated volumetric water content of pile material diffusivity |
| Liner or underlying soil permeability |
| Horizontal hydraulic conductivity of lower layers of pile surface slope |
| Slope of underlying foundation material |
| Pile physical dimensions (height, volume, surface area) |

(2) Tailings and leach solution impoundments. Major mechanisms of gradual release from tailings and leach solution impoundments include seepage through the bottom of the pond to underlying soils and ground water, and overflow of ponds resulting in introduction of acid bearing waters to downstream surface water bodies.

Seepage through the bottom of a pond is most directly related to underlying materials, which can be grouped for the purposes of release assessment into two broad categories: (1) impermeable synthetic liners, and (2) semipermeable liners (clay, compacted soil) and untreated site soils. The first group is assessed through the assumption that seepage is negligible unless the liner fails. Hence, release rate estimation is based on an assessment of likelihood and severity of liner failure. The second group is assessed through the classic methods of estimating fluid flow through soils of various permeabilities. Note that failure of semipermeable liners may also occur (USEPA 1985b), resulting in rates of release greater than predicted through Darcy flow modeling of liner material. The following subsections outline estimations of release rates through both types of liners and due to impoundment overflow.

(a) Releases associated with liner/dam failure. USEPA (1985b) reviewed available literature regarding lined waste facility failure for the purpose of identifying causes of such failure, performing a statistical analysis of failure probability for various facility types, and assessing release severity associated with facility failure.

Specific failure mechanisms affecting surface impoundments were identified from case studies, and the probability and severity of each type of failure tabulated (see Table 3-9). Fault-tree analysis was employed to identify causal relationships among specific operation, design, and environmental parameters, and impoundment failure and release. The probabilities of individual component failures were then quantified based on historical data and engineering judgment. These individual component failure probabilities were used to assess the likelihood and severity of releases from each facility type.

This model was designed for estimation of release probability from a wide variety of liner and impoundment types. It could be modified, however, through the use of design, operation, and environmental parameter ranges (and attendant probabilities of component failure) specific to the mining industry to assess the probability of mine tailings or solution impoundment failure. Probability of releases on a nationwide basis could be predicted to within the confidence level of the method (one to two orders of magnitude), and release estimates on a nationwide basis could be developed. The model is not presently intended for site-specific failure probability analysis;* model developers are investigating this application at this writing.

(b) Release due to seepage through semi-permeable liners. McWhorter and Nelson (1980) present a model for estimating the rate of seepage of fluids through the bottom of a pond having a semi-permeable liner, or no liner. Major parameters affecting the rates of seepage include: thickness and permeability of various layers of material at the pond bottom (potentially including coarse tailings, slimes, and semi-permeable liner); the depth of ponded water; and the permeability of underlying soils (foundation material). Volumetric flux of fluid through the liner is a function of seepage rates and impoundment area. This method is directly applicable to the estimation of acid release from tailings/solution ponds due to seepage. Data requirements are presented in Table 3-10; a considerable amount of site-specific data is required. Methods are presented by McWhorter and Nelson for estimating some parameters, but site-specific data are highly preferable to estimated values.

---

*Personal communication with Donna Perla, Project Officer, Failure and Release Submodel, Liner Location Risk and Cost Analysis Model project, USEPA Office of Solid Waste, Economics Analysis Branch.

175

Table 3-9. Summary of Potential Surface Impoundment Catastrophic Failure Mechanisms

| | |
|---|---|
| Natural event | Freeze/thaw |
| | Wind (erosion) |
| | Permafrost melt |
| | Flooding |
| | Seismic activity (faulting) |
| | Sinkhole collapse |
| Location specific event | Excess runoff (erosion) |
| | Slumping |
| | Vegetative growth |
| | Death of vegetation (loss of cover) |
| | Animal burrowing |
| | Moisture/thermal expansion |
| | Rise of ground-water table |
| | Microbial attack |
| | Wind (wave action) |
| Operation and maintenance | Material aging/life expectancy |
| | Consolidation/subsidence |
| | Ponding or excess hydrostatic forces |
| | Swelling due to moisture |
| | Incompatible waste interaction |
| | Breach of security/vandalism |
| | Silting or clogging |
| | Incompatible waste/component interaction |
| | Volatilization |
| Poor/improper construction | Damage during construction |
| | Insufficient compaction |
| | Improper sizing |
| | Insufficient thickness |
| | Improper sealing |
| | Improper grading and subbase preparation |
| | Non-optimum moisture content of material |
| | Exposure to UV light |
| Poor/improper design | Absence of gas migration trench or vent |
| | Undersizing |
| | Poor material selection (structural weakness) |
| | Inadequate ground-water monitoring |
| | Inadequate thickness |
| | Inadequate slope |
| | Absence of inlet and outflow structures |

Source: USEPA 1985.

Table 3-10. Data Requirements for McWhorter and Nelson Impoundment Seepage Model

| |
|---|
| Project life |
| Area of impoundment |
| Equivalent radius of impoundment |
| Liner thickness |
| Average depth of pond |
| Average thickness of slimes vs. time |
| Average thickness of coarse tailing vs. time |
| Initial saturated thickness of aquifer |
| Initial thickness of unsaturated zone |
| Saturated conductivity of coarse tailings |
| Saturated conductivity of slimes |
| Saturated conductivity of liner |
| Vertical saturated conductivity of foundation |
| Saturated conductivity of aquifer |
| Porosity of foundation materials |
| Description of foundation material |
| Initial water content in foundation |
| Residual water content in foundation |
| Displacement pressure head in foundation |

Source: McWhorter and Nelson 1980.

(c) Release due to overflow of impoundments. The frequency and severity of impoundment overflow are most closely related to: (1) water diversion structures which prevent the flow of runoff from upgradient areas into impoundments; and (2) the freeboard of the impoundment dam system. Where these features are adequately designed (and the pond capacity is adequate to handle the volume of waste or process solution) pond overflow can be effectively eliminated.

Assessment of overflow releases requires consideration of the adequacy of these design features, along with the following additional parameters: local rainfall/snow-melt frequency, duration, and intensity data; infiltration versus runoff fraction for precipitation to the watershed associated with the impoundment (a function of soil types, vegetation, slope); local evapotranspiration rates; and area of watershed and length of longest water course (Hutchinson 1985). These latter data are used to estimate the time of water flow towards the impoundment and the maximum flow rate likely to occur.

It should be noted that although the concentration of acid in the standing water and interstitial waters of a pond is a function of the parameters discussed previously (i.e., those affecting acid formation rates; see Section 3.5.1) the concentration of pond effluent during overflow is affected by numerous additional parameters. Prediction of overflow acid concentration is a data intensive exercise, and may result in low-confidence estimates because of the potentially highly complex nature of bed sediment and water column interactions, water stratification and current patterns within a pond during the overflow event, and the change in acid formation/carbonate dissolution kinetics in the presence of rapid removal mechanisms. HydroQual (1982) presents a simplified model for impoundment concentration which assumes complete mixing within the impoundment, steady-state flow and contaminant introduction rates, and a fixed, uniform bed sediment which interacts with water column contaminants. Parameters that most significantly affect the water column (and effluent) concentration include: loading rate of contaminant to the impoundment; total volumetric flow into the impoundment; residence time of water in the impoundment; and overall rate of contaminant removal from the water column (or, in the case of acid generation by impoundment tailings, acid removal/replacement rate ratio).

### 3.5.3 Conclusions

Estimation of acid releases (with the exception of releases resulting from liner failure) from mining wastes is feasible on a site-specific basis through employment of the techniques described above. However, the foregoing discussion indicates that the development of reliable values for acid release requires much site-specific data; such detailed data were not available in the literature reviewed for any mine sites. The development of source terms for exposure and risk assessment associated with acid generating wastes through modeling of releases would therefore require an extensive data gathering effort for several sites representative of the industry. In view of the effort required for data gathering, and the low reliability of release estimates as compared to empirical data from site monitoring, the assessment of source terms through site monitoring should be investigated as an alternative to modeling.

# 4. REFERENCES

Alesii BA, Fuller WH. 1976. The mobility of three cyanide forms in soils. pp. 213-223. In: Residual Management by Land Disposal. WH Fuller, ed. U.S. Environmental Protection Agency, Cincinnatti, Ohio. NTIS PB 256768.

Bailar JC Jr, Busch DH. 1956. A general survey of the coordination compounds. In: The chemistry of the coordination compounds. JC Bailar, Jr., ed. Reinhold Publishing Corporation, New York.

Bandish O, Bass LW. 1922. Eisen ab licht-chemisher katalyzator. I. Uber die zursetzing von ferrocyankalium in tageslicht. Ber. Deut. Chem. Gesell. 55:2698-2706. As quoted in Callahan et al. (1979).

Bond WR, Rouse JV. 1985. Lysimeters allow quicker monitoring of heap leaching and tailings sites. April 1985: 314-319.

Broderius SJ. 1973. Determination of molecular hydrocyanic acid in water and studies of the chemistry and toxicity to fish of metal cyanide complexes. Ph.D. Dissertation, Oregon State Univ., Corvallis, Oregon. 287p.

Broderius SJ. 1977. Personal communication concerning the fate of cyanides in the aquatic environment. EPA Grant R805291, Dec. 8, 1977. Univ. of Minnesota, St. Paul. As quoted in Callahan et al. (1979).

Burdick GE, Lipschuetz M. 1948. Toxicity of ferro- and ferricyanide solutions to fish and determinations of the cause of mortality. Trans. Amer. Fish. Soc. 78:192-202.

Burt RA. 1981. Rates of acid release from pyritic mine talus and the effects of limestone ameliorants on these rates. Master's Thesis. University of South Caroline Department of Geology.

Callahan MA, Slimak MW, Gabel NW, et al. 1979. Water-related environmental fate of 129 priority pollutants. Washington, DC: Office of Water Planning and Standards, USEPA. EPA-440/4-79-029a, Section I. Introduction and Technical Background; Section II. Chapter 12. Cyanides.

Caruccio FT, Geidel G. 1981. Estimating the minimum acid load that can be expected from a coal strip mine. Proceedings, symposium on surface mining hydrology, sedimentology and reclamation. Lexington, KY: University of Kentucky.

Caruccio FT. 1985. Status report regarding project evaluating methodologies for prediction of acid drainage from mine waste. Submitted to John O. Borkle, Water Engineering Research Laboratory, US Environmental Protection Agency, Cincinnati, OH. November 26, 1985.

Caruccio FT. n.d. Applicability of overburden analytical techniques in the prediction of acid drainages from massive sulfide mines draft report. Columbia, SC: University of South Carolina.

Castric PA. 1975. Hydrogen cyanide, a secondary metabolite of _Pseudomonas aerogmosi_. Can. J. Microbiol. 21:613-618.

Chamberlain PG and Pojar MG. 1981. The status of gold and silver leaching operations in the United States. In: Gold and silver leaching, recovery, and economics. ed. by Schlitt WJ, Larson WC, Hiskey JB. Littleton, CO: Society of Mining Engineers of AIME.

Chamberlain PG and Pojar MG. 1984. Gold and silver leaching practices in the United States. U.S. Bureau of Mines Information Circular 8969.

Charles River Associates. 1985. Estimated costs to the U.S. mining industry for management of hazardous solid wastes. Final Report. Prepared for Div. of Solid Waste Management, U.S. EPA.

Clem BM. 1982. Heap leaching gold and silver ores. Engineering & Mining Journal. April 1982: 68-76.

Coburn SE. 1949. Limits of toxic waste in sewage treatment. Sewage Works J. 2:522.

Coppa LV. 1984. Copper, lead, zinc, gold, and silver waste disposal activities and practices in the United States. Washington, DC: U.S. Department of Interior. Bureau of Mines Open File Report 4-85.

Cruz M, Kaiser A, Rowxhat PG, Fripiat JJ. 1974. Absorption and transformation of HCN on the surface of copper and calcium montmorillonite. Clays Clay Mineral. 22:417-425.

DeVries FW. 1986. DuPont Co. Submittal to Versar Inc. of an anonymous memo: Cyanide Levels in Tailings Solution in Plant in Western Australia.

DuPont. 1985. Memo from AE Jones, Chem. Eng. Sec., Eng. Serv. Div., DuPont to FW De Vries, Chem. & Pig. Dept. concerning heat transfer - cyanide degradation in tailings ponds. Sept. 12, 1985.

Duffey SS, Blum MS. 1977. Phenol and guaiacol: biosynthesis, detoxification, and function in a polydesinid millipede, Oxidus grocillus. Insect. Biochem. 7:57-65.

ERCO. 1984. Hazardous waste identification and listing support. Prepared for Office of Solid Waste. U.S. EPA. Contract No. 68-01-6467.

Ely MF, II. 1986. Letter dated March 18, 1986 to Bentley Gregg, Versar Inc. and final report on American Mine Cleanup and Abatement (dated Dec 26, 1985.)

Enfield CG, Carsel RF, Cohen SZ, Phan T, Walters DM. 1982. Approximating pollutant transport to ground water. Ground Water 20(6) 711-722.

Engineering and Mining Journal. 1981a. Heap leaching revives Montana gold district. January 1981:90-91.

Engineering and Mining Journal. 1981b. Pelletizing aids Tombstone leaching operation. January 1981:94-95.

Englehardt PR. 1985. Long-term degradation of cyanide in an inactive leach heap. In: Cyanide and the Environment, Proceedings of a conference. December 11-14, 1984. Tuscon, AZ, pp. 539-547.

Fox FO. 1984. Reclamation work reclaims gold tailings in the Black Hills of South Dakota. Mining Engineering. November 1984:1543-1549.

Frank SN, Bard AJ. 1977. Heterogeneous photocatalyst oxidation of cyanide ion in aqueous solutions at titantium dioxide powder. J. Amer. Chem. Soc. 99:303-304.

Fuller WH. 1985. Cyanides in the environment with particular attention to the soil. In: Cyanide and the environment, Proceedings of a conference. December 11-14, 1984. Tuscon, AZ, pp. 19-46.

Giedel G. 1979. Alkaline and acid production potentials of overburden material: the rate of release, Reclamation Review 2: 101-107.

Hardy RWF, Knight E Jr. 1967. ATP-dependent reduction of azide and HCN by $N_2$- fixing enzymes of Azotobacter rinelandii and Clostridium pasteurianum. Biochem. Biophys. Acta 139:69-90.

Harries JR, Ritchie AIM. Runoff fraction and pollution levels in runoff from a waste rock dump undergoing pyritic oxidation. Water, Air and Soil Pollution 19:155-170.

Harris R, Knowles CJ. 1983a. Isolation and growth of a *Pseudomonas* species that utilizes cyanide as a source of nitrogen. J. Gen. Microbio. 129:1005-1011.

Harris RE, Knowles CJ. 1983b. The conversion of cyanide to ammonia by extracts of a strain of *Pseudomonas fluorescens* that utilizes cyanide as a source of nitrogen for growth. FEMS Microbiol. Lett. 20:337-341.

Heinen HJ, Peterson DG, Lindstrom RE. 1978. Processing gold ores using heap leach-carbon absorption methods. Washington, DC: Bureau of Mines, U.S. Dept of Interior. Information Circular 8770.

Heming TA, Thurston RV. 1985. Physiological and toxic effects of cyanides to fishes: A review and recent advances. In cyanide and the environment. Proceedings of a conference. December 11-14, 1984. Tuscon, AZ, pp. 85-104.

Hendrix J, Nelson JH, Ohmadiantehrani M. 1985. Fate of cyanide tailings - An update. In: Cyanide and the environment, Proceeding of a conference December 11-14, 1984. Tuscon, AZ, pp. 265-272.

Hendrix JL. 1985. Univ. of Nevada Reno. Quarterly Report submitted to U.S. Bureau of Mines, Nov. 4, 1985. Grant Title: Investigation of the rate of cyanide (sic) in precious metals mill tailings impoundments.

Hogan DK, Fitch DC, Scheffel RE, Welch MR. 1982. Escalante: Major silver mine nears first year of full operation. Engineering and Mining Journal. September 1982: 1323-1327, 1378.

Huiatt JL. 1985. Cyanide from mineral processing: problems and research needs. In: Cyanide and the environment, vol 1. D. van Zyl, ed., Fort Collins, Colorado: Geotechnical Engineering Program, Dept. of Civil Engineering, Colorado State Univ. pp. 65-81.

Hutchinson I. 1985. Surface water control. In: Course text for short course on evaluation, design, and operation of precious metal heap leaching projects, presented October 13-15, 1985 in Albuquerque, NM. Littleton, CO: Society of Mining Engineers.

Hutchinson SA. 1973. Biological activities of fungal metabolites. Am. Rev. Phytopathol. 11:233-246.

HydroQual, Inc. 1982. Application guide for CMA - HydroQual chemical fate models. Prepared for: Chemical Manufacturers Association, Washington, DC.

Intermountain Soils, Inc. 1985. Environmental handbook for cyanide leaching projects. Ed. by Stanton MD, Colbert TA, Treholme RB. For Energy, Mining and Minerals Div., National Park Service, U.S. Department Interior.

Jackson D. 1982. How Duval transformed its Battle Mountain properties from copper to gold production. Engin. Min. Jour. Oct. 1982:95-99.

Jaynes DB, Rogowski AS, Poinke HB. 1984a. Acid mine drainage from redrained coal strip mines: 1. Model description. Wat. Res. Research 20(2):233-242.

Jaynes DB, Poinke HB, Rogowski AS. 1984b. Acid mine drainage from reclaimed coal strip mines: 2. Simulation results of model. Wat. Res. Research 20(2): 243-250.

Jolly JLW. 1983 Zinc. In: 1983 Bureau of Mines Minerals Yearbook. Washington, DC: U.S. Department of Interior.

Jolly JLW, Edelstein DL. 1984. Copper. In: 1984 Bureau of Mines Minerals Yearbook. Washington, DC: U.S. Department of Interior.

Jolly JLW. 1985. Copper. In: 1985 U.S. Bureau of Mines, Mineral Facts and Problems. Washington, DC: U.S. Department of Interior Bureau of Mines Bulletin 675.

Jolly JLW. 1985b. Zinc. In: 1985 U.S. Bureau of Mines, Mineral Facts and Problems. Washington, DC: U.S. Department of Interior Bureau of Mines Bulletin 675.

Kostenbalder PD, Flecksteiner JW. 1969. Biological oxidation of coke plant weak ammonia liquor. J. Water Pollut. Control Fed. 41:199-207.

Kreible VK, McNally JG. 1929. The hydrolysis of hydrogen cyanide by acids. J. Amer. Chem. Soc. 51:3368-3375.

Lorck H. 1948. Production of hydrocyanic acid by bacteria. Physiol. Plant. 1:142-146.

Lucas JM. 1984. Gold. In: 1983 Bureau of Mines Mineral Yearbook. Washington, DC: U.S. Department of Interior.

Lucas JM. 1985a. Gold. In: 1984 Bureau of Mines Mineral Yearbook. Washington, DC: U.S. Department of Interior.

Lucas JM. 1985b. Gold. In: 1985 U.S. Bureau of Mines Mineral Facts and Problems. Washington, DC: U.S. Department of Interior Bureau of Mines Bulletin 675.

Ludzack FJ, Schaffer RB. 1962. Activated sludge treatment of cyanide, cyanate, and thiocyanate. J. Water Pollut. Control Fed. 34:320-341.

Martin HW, Mills WR, Jr. 1976. Water pollution caused by inactive ore and mineral mines: a national assessment. Cincinnati, OH: U.S. Environmental Protection Agency, Office of Research and Development. EPA 600/2-76-298.

McClelland GE, Eisele JA. 1982. Improvements in heap leaching to recover silver and gold from low-grade resources. Washington, DC: Bureau of Mines, U.S. Department of Interior. Report of Investigations 8612.

McGrew KJ. 1985. Wharf Resources (USA), Inc. letter to Robert Townsend, Program Chief, DWNR, Exploration and Mining Program, State of South Dakota, concerning 1984 Test Site Neutralization Status Report, dated Jan. 28, 1985.

McQuiston FW, Jr., Shoemaker RS. 1981. Gold and silver cyanidation plant practice. Vol. 2. New York: American Institute Mining Metallurgical and Petroleum Engineers, Inc.

McWhorter DB, Nelson JD. 1980. Seepage in the partially saturated zone beneath tailings impoundments. Mining Engineering 32(4):432-439.

Milligan DA. 1985a. Cyanide destruction. Chapter 14. In Evaluation, design, and operation of precious metal heap leaching projects. October 13-15, 1985. SME-AIME Fall Meeting. Albuquerque, NM.

Milligan DA. 1985b. Solution Control. Chapter 10. In Evaluation, Design, and Operation of Precious Metal Heap Leaching Projects. October 13-15, 1985, SME-AIME Fall Meeting. Alburquerque, NM.

James M. Montgomery, Consulting Engineers, Inc. 1986. Letter to Docket Clerk, RCRA Docket, OSW, EPA. Comments on EPA Report to Congress "Wastes from Extraction and Beneficiation of Metallic Ores, Phosphate, Rock, Asbestos, Overburden from Uranium Mining, and Oil Shale"; letter dated March 26, 1986, signed by Rick Richins.

Moore J. 1986. U.S. Bureau of Mines. Div. of Nonferrous Metals. Personal communication concerning cyanidation wastes generated from 1974 to 1978, in memo to Bentley Gregg, Versar Inc., dated Feb. 7, 1986.

185

Moore JW, Sutherland DJ, Beaubien VA. 1979. Algal and invertebrate communities in three subarctic lakes receiving mine wastes. Water Res. 13:1193-1202.

Morth AH, Smith, EE, Shumate, KS. 1972. Pyritic systems; a mathematical model. Washington, DC: U.S. Environmental Protection Agency Office of Research and Monitoring. PB213 887.

Newhouse WH. 1969. Ore deposits as related to structural features. Princeton, NJ: Princeton University Press.

Nowak E, Chmielowski J. 1975. Study of the biochemical decomposition of cyanide by microorganisms. Biochem. Ochr. Srdowiska Nat., Mater. Ses. Nauk. pp.109-116 (Abstract only). CA 92:88494x (1980).

Oi S, Yamamoto T. 1977. A Streptomyces species effective for conversion of cyanide into thiocyanate. J. Ferment. Technol. 55:560-569. (Abstract only). CA 88:85729j (1978).

PEI (PEDCo Environmental, Inc.) 1983. Evaluation of management practices for mine solid waste storage, disposal, and treatment. Volume I. Characterization of mining industry wastes. Cincinnati, OH: U.S. Environmental Protection Agency Office of Research and Development. Contract No. 68-03-2900.

PEI (PEDCo. Environmental, Inc.) 1984. Survey and evaluation of acid drainage from mining and storage, disposal and treatment of mine solid waste. EPA 68-03-2900. Draft Report. IERL. Cincinnati, OH: U.S. Environmental Protection Agency.

Pahlman JE. 1986. U.S. Bureau of Mines, letter to Bentley Gregg, Versar Inc. concerning cyanide levels in Tombstone Silver Mines Inc. spent heap leach ores, dated March 28, 1986.

Phillips LF. 1978. Pressure dependence of the rate of reaction of OH with HCN. Chem. Phys. Lett. 59:538-539.

Potter W, Chang, BK, Adler, D. 1982. The effects of air pollution and acid rain on fish, wildlife, and their habitats. U.S. Department of the Interior, FWS 14-16-009-80-085.

Raef SF, Characklis WG, Kossich MA, Ward CH. 1977a. Fate of cyanide and related compounds in aerobic microbial systems. I. Chemical reaction with substrate and physical removal. Water Res. 11:477-483.

Raef SF, Characklis WG, Kossich MA, Ward CH. 1977b. Fate of cyanide and related compounds in aerobic microbial systems. II. Microbial degradation. Water Res. 11:485-492.

Ray WR. 1985. A simple leach procedure for determining the total cyanide content of heap leach tailings. In: Cyanide and the environment. Proceedings of a conference. December 11-14, 1984. Tuscon, AZ, pp. 201-211.

Reed RE. 1985. Cyanide compounds in plants and their effects on animals. In: Cyanide and the environment, vol. 1. D. van Zyl, ed. Geotechnical Engineering Program, Dept. of Civil Engineering, Colorado State University. pp. 47-51.

Reese RJ, Jr. 1984. Silver. In: 1983 Bureau of Mines Mineral Yearbook. Washington, DC: U.S. Department of Interior.

Reese RJ, Jr. 1985a. Silver. In: 1984 Bureau of Mines Mineral Yearbook. Washington, DC: U.S. Department of Interior.

Reese RJ, Jr. 1985b. Silver. In: 1985 U.S. Bureau of Mines Mineral Facts and Problems. Washington, DC: U.S. Department of Interior, Bureau of Mines Bulletin 675.

Ridge JD, ed. 1970. Ore deposits of the United States, 1933-1967. Vol. 2. New York: The American Institute of Mining, Metallurgical, and Petroleum Engineers, Inc.

SCS Engineers, Inc. 1985. Summary of environmental incidents from the disposal of mining wastes. Prepared for the Office of Solid Waste, U.S. EPA. Contract No. 68-01-7053.

SRI. 1985. Stanford Research Institute International. 1985 Directory of chemical producers, United States of America. Menlo Park, CA: SRI International. pp. 640, 867.

Schenk B, Wilke BM. 1984. Cyanidadsorption on sesquioxiden, tonmineralen und huminstoffen. Z. Pflanzenernaehr. Bodenk. 147:669-679.

Schiller JE. 1983. Removal of cyanide and metals from mineral processing waste waters. Washington, DC: Bureau of Mines, U.S. Department of Interior, Department of of Investigations. 8836.

Schlitt WJ, ed. 1982. Interfacing technologies in solution mining: proceedings of the second SME-SPE international symposium Denver, Colorado. November 18-20, 1981. Hoboken, NJ: Lucas-Guinn Co.

Schmidt JW, Simovic L, Shannon EE. 1981a. Development studies for suitable technologies for the removal of cyanide and heavy metals from gold milling effluents. Proc. 36th Indust. Wastes Conf. Purdue Univ. pp.831-846.

Schmidt JW, Simovic L, Shannon E. 1981b. Natural degradation of cyanides in gold milling effluents. Presented at Cyanide and the gold mining industry seminar, January 22-23, 1981. Ottawa, Canada.

Schwarz R, Tede K. 1927. Uber die photochemie der komplexverbindungen. III. Die hexacyanokomplexe des dreiwertigen essins, kabalts, chroms, mangans. Ber. Deut. Chem. Gesell. 60:69-72. As quoted in Callahan et al. (1979).

Scott JS, Ingles JC. 1981. Removal of cyanide from gold mill effluents. Prepared for Canadian mineral processors thirteenth annual meeting. January 20-22, 1981. Ottawa, Canada.

Scott JS. 1985. An overview of cyanide treatment methods for gold mill effluents. In: Cyanide and the environment. Proceedings of a conference. December 11-14, 1984. Tucson, AZ, pp. 307-330.

Sheffer HW, Evans LG. 1968. Copper leaching practices in the western United States. Washington, DC: U.S. Department of Interior Circular 8341.

Simovic L, Snodgrass WJ, Murphy KL, Schmidt JW. 1985. Development of a model to describe the natural degradation of cyanide in gold mill effluents. In: Cyanide and the environment. Proceedings of a conference. December 11-14, 1984. Tucson, AZ, pp. 413-432.

Simovic L, Snodgrass WJ. 1985. Natural removal of cyanides in gold milling effluents - Evaluation of removal kinetics. Water Poll. Res. J. Canada. 20:120-135.

Simovic L. 1984. Report on natural degradation of cyanides form the Cullaton Lake gold mines effluent. Research report. Burlington, Ontario: Environment Canada. Environment Protection Service, Wastewater Technology Center.

Singh HB, Jaber HM, Davenport JE. 1984. Reactivity/volatility classification of selected organic chemicals: existing data. Research Triangle Park, NC: Environmental Sciences Research Laboratory, U.S. Environmental Protection Agency. EPA 600/3-84-082. NTIS PB 84-232883.

188

Sobek AA, Schuller WA, Freeman JR, and Smith RM. 1978. Field and laboratory methods applicable to overburdens and mine soils. Cincinnati, OH: U.S. Environmental Protection Agency Office of Research and Development. EPA 600/2-78-054.

Sprague JC. 1986. Barrick Mercur Gold Mines, Inc. letter to Bentley Gregg, Versar Inc. concerning cyanide levels in old Golden Gate mill tailings piles, dated April 2, 1986.

Stampfli S. 1986. Wharf Resources (USA) Inc. letter to Robert Townsend, Director, OWNR, Exploration and Mining Program, State of South Dakota, concerning 1985 Ambient Air Cyanide Monitoring, dated Feb. 12, 1986.

TRC Environmental Consultants Inc. 1985. Review of the SCS damage case study. Prepared for American Mining Congress. TRC Project No. 2896-N11-00.

Towill LE, Drurg JS, Whitfield BL, Lewis EB, Galyan EL, Hammons AS. 1978. Reviews of the environmental effects of pollutants. V. Cyanide. pp. 11-33. Oak Ridge, TN: Oak Ridge National Laboratory, NTIS PB 289 920.

Turk TW, Sass SA. 1984. Engineering design of the Mercur Gold Project ore processing facility. Mining Engineering. November, 1984:1563-1567.

USBM (US Bureau of Mines) Minerals Yearbook. Various years. Washington, DC: U.S. Department of the Interior.

USEPA. 1976. Quality criteria for water, cyanide. Washington, DC: U.S. Environmental Protection Agency, Office of Water Planning and Standards.

USEPA. 1979. Methods for chemical analysis of water and wastes. Method 335. Cincinnati, OH: U.S. Environmental Protection Agency, Office of Research and Development.

USEPA. 1982. Test methods for solid wastes. SW846, 2nd ed. Washington, DC: U.S. Environmental Protection Agency, Office of Solid Waste.

USEPA. 1983. Revised section B of ambient water quality criteria for cyanide. Aquatic toxicology. Draft. Washington, DC: USEPA.

USEPA. 1985a. Report to Congress on wastes from the extraction and beneficiation of metallic ores, phosphate rock, asbestos, overburden from uranium mining, and oil shale. U.S. Environmental Protection Agency Office of Solid Waste, Economic Analysis Branch. October 28, 1985 draft.

USEPA. 1985b. Draft report. Liner location risk and cost analysis model; Appendix A: failure and release submodel. Washington, DC: US Environmental Protection Agency Office of Solid Waste, Economics Analysis Branch. (Contract 68-01-6621).

USGS/CDMG/USBM. 1966. Mineral and water resources of California. Report of the U.S. Geological Service in collaboration with California Division of Mines and Geology and the U.S. Bureau of Mines, to Committee of Interior and Insular Affairs, U.S. Senate. Washington, DC: U.S. Government Printing Office.

Ware GC, Painter HA. 1955. Bacterial utilization of cyanide. Nature 175:900.

Weast RC, ed. 1977. CRC Handbook of chemistry and physics, 58th Edition, CRC Press: Cleveland, Ohio.

Wharf Resources Inc. 1982. Annie Creek Project Small Column Neutralization Tests and Native Soil Neutralization Tests. Internal report dated Oct. 10, 1982.

White L. 1977. Heap leaching will produce 85,000 oz/year of dore bullion for Smoky Valley Mining. Engineering and Mining Journal. 178(7):70-72.

Wiegand GH, Tremelling M. 1972. The kinetics and mechanism of the decomposition of potassium cyanide in aqueous alkaline medium. Hydrolysis of the simplest nitrile, HCN. J. Org. Chem. 37:914-916.

Willard RJ. 1984. Mining and quarrying trends in the metal and non-metal industries. In: 1984 Bureau of Mines Minerals Yearbook. Washington, DC: U.S. Department of Interior.

Wissing F. 1974. Cyanide formation from oxidation of glycine by a Pseudomonas species. J. Bacteriol. 117:1289-1294.

Woodbury WD. 1983. Lead. In: 1983 Bureau of Mines Minerals Yearbook. Washington, DC: U.S. Department of Interior.

Woodbury WD. 1984. Lead. In: 1984 Bureau of Mines Minerals Yearbook. Washington, DC: U.S. Department of Interior.

Woodbury WD. 1985. Lead. In: 1985 U.S. Bureau of Mines Mineral Facts and Problems. Washington, DC: U.S. Department of Interior Bureau of Mines Bulletin 675.

Young AR. 1986. Sunshine Mining Co. letter to Dexter Hinckley, OSW, EPA concerning cyanide levels in potable well water and water seepage into shallow wells, dated March 17, 1986.

van Zyl D, ed. 1985. Cyanide and the environment, vol. 1 and 2. Fort Collins, Colorado: Geotechnical Engineering Program, Dept. of Civil Engineering, Colorado State University.